Respiratory exposure to hazardous chemical substances during additive manufacturing using nylon and alumide

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This mini-dissertation is dedicated to my
mother who have always supported me and
loved me unconditionally.

PREFACE

This mini-dissertation is submitted in article format and is written according to the requirements outlined in the journal Annals of Work Exposure and Health. Therefore, the literature is referenced according to the style presented by Annals of Work Exposure and Health. Examples of references:

Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs) - Development of practical criteria for mist sampling. Ann Occup Hyg; 44: 165–72.
Vincent JH. (1989) Aerosol sampling: science and practice. Chichester, UK: John Wiley. ISBN 0471921750.
Swift DL, Cheng Y-S, Su Y-F, Yeh H-C. (1994) Ultrafine aerosol deposition in the human nasal and oral passages. In Dodgson J, McCallum RI, editors. Inhaled Particles VII. Oxford: Elsevier Science. p. 77–81. ISBN 0 08 040841 9 H.
British Standards Institution. (1986). BS 6691: 1986. Fume from welding and allied processes. Part 1. Guide to methods for the sampling and analysis of particulate matter. London: British Standards Institution.
Morse SS. (1995) Factors in the emergence of infectious diseases. Emerg Infect Dis [serial online] 1995 Jan–Mar;1(1). Available from: URL: http://www.cdc.gov/ncidod/EID/eid.htm (accessed 25 Oct 2010).

This referencing style was used throughout the mini-dissertation. This mini-dissertation is written according to British English spelling. The outline of this mini-dissertation is as follows:

Chapter 1: Introduction which introduces the study and states the aims, objectives and hypotheses.
Chapter 2: Literature study which focusses on all literature relevant to this study.
Chapter 3: An article on the respiratory exposure to hazardous chemical substances during additive manufacturing using nylon and alumide.
Chapter 4: A concluding chapter which lists the main findings, limitations, recommendations and suggestions for future studies.

AUTHORS' CONSTRIBUTIONS

Name	Contributions
Ms. B Visagie	• Planning of study. • Conducting literature research. • Execution of monitoring. • Interpretation of results. • Conducting statistical analyses. • Formulation of recommendations. • Writing of mini-dissertation.
Dr. SJL Linde	• Supervisor. • Assisted with approval of study protocol, design and planning of study, interpretation of results, selection of statistical analysis methods and review of the mini-dissertation.
Prof. JL du Plessis	• Co-supervisor. • Assisted with approval of study protocol, design and planning of study, interpretation of results, selection of statistical analysis methods and review of the mini-dissertation.
Mrs. S du Preez	• Co-supervisor. • Assisted with approval of study protocol, design and planning of study, interpretation of results, selection of statistical analysis methods and review of the mini-dissertation.
Prof. DJ de Beer	• Assistant supervisor • Facilitated collaboration between the NWU and Facility A and B where the study was performed. • Provided technical guidance on additive manufacturing processes.

The following is a statement from the co-authors that confirms each individual’s role in the study:

I declare that I have approved the articles and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of B Visagie’s M.Sc (Occupational Hygiene) mini-dissertation.

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ABSTRACT

Title: Respiratory exposure to hazardous chemical substances (HCSs) during additive manufacturing using nylon and alumide.

Background: In the additive manufacturing (AM) industry there is very little information available regarding the area emission of and personal exposure to HCSs [particulates, metals and volatile organic compounds (VOCs)] during selective laser sintering (SLS), utilising nylon and alumide. It is possible that HCSs are emitted into the air during the pre-processing, processing and post-processing activities, which could lead to respiratory exposure, followed by the development of adverse health effects.

Aims: To determine the physical and chemical composition of both virgin (new) and used nylon and alumide. In addition, the aim was also to determine the area emission of and personal respiratory exposure to HCSs that take place during SLS utilising nylon and alumide powder.

Methodology: The physical and chemical composition of virgin and used nylon [nylon-12 (PA2200)] and alumide was determined with particle size distribution (PSD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF) analysis. Area emission of particle size fractions 0.01 µm to > 1µm was determined with a TSI Model 3007 Condensation Particle Counter (CPC) (TSI Inc., Shoreview, Minnesota, USA), while the area emission concentration with a particle size range of 0.3 – 10 µm was determined with a TSI AeroTrak^{TM} Airborne Particle Counter (APC) (TSI Inc., Shoreview, Minnesota, USA). National Institute for Occupational Safety and Health (NIOSH) Methods 0500 and 7300 were used to determine the area emission of and personal exposure to inhalable and respirable sized nylon and alumide dust. A Gillian Gilair Plus sampling pump (Sensidyne, Clearwater, Florida, USA) was calibrated to a flow of 2 L/min and connected to an Institute of Occupational Medicine (IOM) sampler to determine the inhalable and respirable sized nylon and alumide dust. Personal Nanoparticle Respiratory Deposition (NRD) samplers were connected to Gillian Gilair sampling pump calibrated to a flow of 2.5 L/min to determine the personal exposure of AM operators to particles < 300 nm. Traceair VOC badges were used to determine the area emission of and personal exposure to VOCs during all three phases of SLS utilising nylon and alumide.

Results: PSD results indicated that all virgin and used nylon and alumide fell into the inhalable particle size range (63.85 - 65.30 µm) and that the measured PSD differed from the particle sizes listed in the Material Data Sheets (56 µm – 60 µm). There were no statistical significant differences ($p < 0.05$) found between the volume weighted mean particle sizes of virgin (new) and used nylon and alumide powders. The SEM analyses also confirmed that there were no visible differences in the size and shape between virgin and used nylon and alumide. XRF analyses found that virgin powders consisted of 39% of aluminium (Al), while used powders consisted of 51% of Al. An increase in particle number concentration was identified during all three phases of AM, when compared to the corresponding ambient readings. An increase in particle number concentrations were identified for specific activities, such as machine cleaning, powder mixing, machine warm-up, build removal and removal of excess powders from the build. For all APC results, the 0.30 µm particle size fraction indicated the highest concentration compared to 0.5, 1, 3, 5 and 10 µm. During gravimetric area emission sampling of SLS utilising nylon over an entire shift, low concentrations of inhalable and respirable sized dust was detected, while the results for SLS using alumide was below the detection limit. The personal exposure results indicated that the highest concentration of exposure to inhalable sized nylon and alumide dust took place during the post-processing activities (5.52 mg/m^3 and 5.32 mg/m^3). The personal exposure to respirable sized nylon and alumide dust only took place during post-processing activities (0.18 mg/m^3 and 0.59 mg/m^3). All personal particulate exposures were below the respective OELs for total inhalable and respirable dust. Small concentrations of particles < 300 nm were also detected during SLS using alumide. Aluminium (Al), iron (Fe), titanium (Ti) and zinc (Zn) were metals found in personal and area samples during SLS with alumide. Acetone, pentane, chloroform, toluene and naphthas were the VOCs detected during area emission and personal exposure during SLS utilising nylon and alumide. All personal exposures to VOCs were well below respective OELs.

Conclusions: This study confirmed that HCSs (particulates, metals and VOCs) are emitted into the workplace atmosphere during SLS with nylon and alumide. However, the concentration HCSs emitted were very low according to standards. AM operators experienced personal exposure to these HCSs (particulates, metals, and VOCs) during this process, especially during post-processing.

It was recommended that a portable local extraction ventilation (LEV) system should be used, especially for manual handling of powders during pre- and post-processing activities to be able to capture particles before they become airborne. Isolation of machines were also recommended to minimise the concentration of particles emitted. Cleaning protocols and personal hygiene measures are two important administrative control measures which should be revised.

Keywords: Nylon, alumide, selective laser sintering, particle size fraction, hazardous chemical substances, area emission, personal exposure.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	percentage
<	smaller than
>	larger than
nm	nanometre
mg/m^3	milligram per cubic metre
p/m^3	particles per cubic metre
p/min	particles per minute
µm	micrometre
µg/h	microgram per hour
AM	additive manufacturing
ABS	acrylonitrile butadiene styrene
Al	aluminium
APC	airborne particle counter
ASTM	American Society for Testing and Materials
BDL	below detection limit
Ca	calcium
CAD	computer-aided design
CEN	European Committee for Standardization
CNS	central nervous system
CO_2	carbon dioxide
CPC	condensation particle counter

DED	direct energy deposition
DMLS	direct metal laser sintering
EBM	electron beam melting
EOS	Electro-Optical System
EU	European Union
FDM^{TM}	fused deposition modelling
Fe	iron
HCS	hazardous chemical substances
HCSR	Hazardous Chemical Substances Regulations
HSE	Health and Safety Executive
LOM	laminated object manufacturing
MDS	material data sheet
NIOSH	National Institute for Occupational Safety and Health
NRD	nanoparticle respiratory deposition
NT	nanotracers
OEL	occupational exposure limit
OEL-RL	occupational exposure limit – recommended limit
OSHA	Occupational Health and Safety Administrative
PA	polyamides
PBF	powder bed fusion
PCTPE	plasticised copolyamide thermoplastic elastomer
PLA	polylactic acid
PEL	permissible exposure limit

PSD	particle size distribution
ROS	reactive oxygen species
SDS	safety data sheet
SEM	scanning electron microscopy
SLM	selective laser melting
SLS	selective laser sintering
STL	stereolithography
Ti	titanium
TWA	time weighted average
3D	three-dimensional
2D	two-dimensional
UFP	ultrafine particle
viz	in other words
VOC	volatile organic compound
XRF	X-ray fluorescence
WEL	workplace exposure limit
Zn	zinc

Chapter 1: Introduction

1.1 Introduction

Additive manufacturing (AM), also known as rapid prototyping or three-dimensional (3D) printing, dates back to the 1960s and, has since, grown into an industry presenting continuous growth and potential (Wohlers and Caffrey, 2015). AM is the process where printer technology is used to join materials, layer by layer, to create 3D objects (Wohlers and Caffrey, 2015; ASTM, 2016; Rayna and Striukova, 2016). Companies have started to implement the process of AM, since the cost of manufacturing is greatly reduced and the products, being supplied through AM, are of superior quality (Wohlers and Caffrey, 2015). AM also provides possibilities to complete work in shorter periods of time as opposed to other manufacturing techniques taking weeks, months or even years (Deak, 1999). This industry has improved the manufacturing process of products such as mobile phones, power tools, aircraft parts and medical implants and therefore, medical industries, aerospace companies and automotive industries are progressively employing AM (Campbell *et al*., 2012; Wohlers and Caffrey, 2015).

Sheet lamination, direct energy deposition (DED), material jetting, material extrusion, binder jetting, powder bed fusion (PBF) and vat photopolymerisation are the seven process categories of AM (ASTM, 2016). These process categories display clear differences regarding their advantages and limitations in terms of quality, build speed and feedstock used (Conner *et al*., 2014). PBF is an AM process category where powder feedstock, such as metals and polymers, are melted through thermal energy and thereafter, cooled to form a solid object. Selective laser sintering (SLS), electron beam melting (EBM) and direct metal laser sintering (DMLS) represent different technologies of PBF (Wohlers and Caffrey, 2015).

SLS is capable of using a variety of feedstock, such as nylon, alumide, sand and silver (Kruth *et al.*, 2003; De Beer *et al*., 2012; Wohlers and Caffrey, 2015). Polymer (plastic) powders, with carbon-carbon bonds, are separated into different classes such as polyamides (PA), polypropylene and polystyrene (Gibson and Shi, 1997; Chung *et al*., 2015; Wohlers and Caffrey, 2015). Nylon is classified as a synthetic polyamide and is commonly used during SLS and is also classified as a thermoplastic. Thermoplastics can be melted and cooled repeatedly without any of the material properties being lost (Wohlers and Caffrey, 2015). Nylon-6 (PA 6), nylon-11 (PA 11) and nylon-12 (PA 12) are different types of nylon utilised during SLS (Tiwari and Pande, 2013). In order to improve material properties, metal powders can be added to polymer (plastic) powders to create metal-polymer powders. For example, nylon (PA2200) and aluminium can be combined to create alumide (Combrink *et al*., 2012; De Beer *et al*., 2012; Wohlers and Caffrey, 2015). This study focuses on SLS utilising nylon and alumide.

AM processes consist mostly of three main phases identified as pre-processing, processing and post-processing (Aubin, 1994). A computer-aided design (CAD) is created during the pre-processing phase after which a stereolithography (STL) format is created from the CAD design format (Aubin, 1994; Mahindru and Mahendru, 2013). Then the AM machine is prepared by the AM operator during which the build chamber is cleaned, powders are sieved and powder bins are filled (Elliott and Love, 2016). After the pre-processing has been completed, the processing phase (build phase) follows in the enclosed build chamber. At this stage, the interaction of the AM operator with the AM machine is limited to build monitoring (Aubin, 1994; Elliott and Love, 2016). During the processing phase, the build plate inside the AM machine is coated with a layer of polymer powder, followed by the fusing of the powders by a carbon dioxide (CO_2) laser. Then a new powder layer is applied (Scholten and Christoph, 2001; Wong and Hernandez, 2012; Mahindru and Mahendru, 2013). The intended object, contained inside a block and covered with powders, is created after the predetermined number of cycles are finished (Scholten and Christoph, 2001). During the post-processing phase, the printed object is manually removed from the build chamber and the excess powders are removed. The object is sanded, ground, polished or painted by the AM operator to improve the appearance and durability of the build (Deak, 1999; Scholten and Christoph, 2001; Mahindru and Mahendru, 2013; Elliott and Love, 2016). Objects made of alumide react better than those made of polymers, such as PA 12, during the phase of post-processing where sanding, grinding and polishing are performed on the object (Deak, 1999; De Beer *et al*., 2012). Exposure to AM powders is more likely to occur during the manual handling of the powders which takes place during the pre-processing and post-processing phases (Graff *et al*., 2016). Very little information is available regarding the potential exposure of AM operators during these required SLS activities being performed with nylon and alumide.

When investigating the effects of airborne particles on human health, it is important to consider the concentration, shape and size of the relevant particles (Cherrie and Aitken, 1999). The behaviour of particles within the respiratory tract is affected by the shape of the relevant particles. The types of shapes found are isometric, fractal, platelet or spherical. The aerodynamic diameter of a particle is another important factor to consider when examining the behaviour of particles (Brosseau and Lungu, 2005). To re-use unsintered powders from previous AM builds, virgin (new) powders must be combined with the used powders, because the mechanical and thermal properties are altered when the powders are heated (Wohlers and Caffrey, 2015). Inhalable, thoracic and respirable particle size fractions need to be considered during respiratory exposure to airborne particles, because the size fraction could influence the adverse health effects that could arise. Inhalable mass fractions can penetrate to the mouth and nose following inhalation while thoracic sized particles can penetrate beyond the larynx up to the upper regions of the bronchioles and respirable sized particles can penetrate to the unciliated alveoli sacs due to differences in aerodynamic diameter (CEN, 1993; Brown *et al*., 2013).

According to the European Standard, EN481:1993 (Workplace atmospheres – Size fraction definitions for the measurement of airborne particles) and Brown *et al*. (2013), particles can be classified in terms of mass fraction. These definitions classify the inhalable dust size fraction as a particle size having 50% penetration (cut-point) into the nose and mouth (an aerodynamic diameter of less than 100 µm), the thoracic dust size fraction as a particle size having 50% penetration (cut-point) into the upper regions of the bronchioles (an aerodynamic diameter of particles less than 10 µm) and the respirable dust size fraction as a particle size having 50% penetration (cut-point) into the unciliated alveoli sacs (an aerodynamic diameter of less than 4 µm) (CEN, 1993; Brown *et al*., 2013). These cut-points are used to define the performance of the aerosol samplers and to link a size fraction to the particles that will probably enter each area of the respiratory system.

Ultrafine particles (UFPs) have an aerodynamic diameter smaller than 100 nm (Oberdörster and Utell, 2002) and are emitted from desktop fused deposition modelling (FDM^{TM}) printers using feedstock such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and nylon filaments or cartridges (Kim *et al.*, 2015; Azimi *et al*., 2016; Stabile *et al.,* 2016; Steinle, 2016; Yi *et al*., 2016; Zontek *et al.*, 2016; Kwon *et al*., 2017; Zhang *et al*., 2017). Volatile organic compound (VOC) emission also takes place from desktop FDM^{TM} printers, while utilising PLA, ABS and nylon filaments (Azimi *et al*., 2016; Steinle, 2016; Wojtyla *et al*., 2017). Wojtyla *et al*. (2017) detected VOCs, such as cyclopentanone and propylene glycol during AM utilising nylon, while Azimi *et al.* (2016) indicated the emission of caprolactam, when utilising a nylon-6 based filament, namely plasticised copolyamide thermoplastic elastomer (PCTPE). Wojtyla *et al*. (2017) reported the emission of VOCs after the heating of nylon filaments to different temperatures. Studies found that thermal degradation of nylon filaments starts at 390 °C and cyclopentanone and propylene glycol were the two VOCs emitted. Irritation of the throat and eyes are caused by exposure to propylene glycol and ε-caprolactam (Wieslander *et al*., 2001; Ziegler *et al*., 2008).

Particulate emissions from desktop 3D printers could lead to exposure of the operators operating the AM machines (Graff *et al*., 2016). Graff *et al*. (2016) indicated the generation of submicron sized particles during the use of an industrial AM machine for SLM, utilising metals. Fang *et al.,* (2010) reported a strong correlation between the exposure to particulate matter and the development of ischemic heart disease, systemic inflammation and heart rate variability. Stefaniak *et al*. (2017) reported the increase in mean arterial pressure in rats after respiratory exposure to particles with an aerodynamic diameter of 70 nm, from a desktop 3D printer. This increase in mean arterial pressure was followed by systemic microvascular dysfunction. Airway inflammation and impaired lung function are associated with respiratory exposure to UFPs (Strak *et al*., 2012). UFPs could also lead to membrane perturbation, protein misfolding and generation of reactive oxygen species (ROS) after being deposited in the body (Elsaesser and Howard, 2012). After respiratory exposure to submicron particles, they can penetrate to the alveoli of the lungs and then move into the blood circulation system (Izhar *et al*., 2016). Exposure of human alveolar cells to submicron particles will change the structure and the function of these cells, because the cells' organelles, such as the mitochondria and ribosomes get damaged (Mazzarella *et al.,* 2014). Zhu *et al.* (2008) indicated that submicron sized particles could cause oxidative stress and acute lung damage after a study conducted on rats. A recent study found that nylon exposures can possibly lead to the development of a rare form of pneumoconiosis, called nylon flock worker's lung (Johannes *et al*., 2016). Aluminium is widely known as a neurotoxicant and a variety of conditions, such as impaired renal functions, dementia and Parkinson's disease, are associated with exposure to aluminium (Kawahara *et al*., 2007; Exley, 2014).

A wide range of studies report emissions of hazardous chemicals from desktop FDM^{TM} printers, but only a few studies report emissions from industrial printers. Because desktop FDM^{TM} printers have the ability to release particles (including UFPs) and VOCs into the air, it could be an indication that this occurrence is also possible for industrial AM leading to exposure of AM operators to various hazardous chemicals. Additionally, although there are studies reporting emissions from desktop 3D printers while utilising nylon, there is no emission studies available for alumide. It is therefore justified to conduct a study to assess the emission of and respiratory exposure to various hazardous chemical substances (HCS) (particulates, metals and VOCs) during AM with nylon and alumide to determine the potential health risks to AM operators resulting from respiratory exposure to these compounds.

1.2 Aims and objectives

The aim of this study is to determine the physical and chemical characteristics of powders as well as the emission of and personal respiratory exposure to HCSs (particulates, metals and VOCs) during SLS, utilising nylon and alumide powders, at two AM facilities in South Africa.

The specific objectives of the study are:

1 To assess the physical characteristics (size and shape) and chemical composition of virgin (new) and used nylon and alumide powders from two AM facilities.

2 To assess the airborne concentration of particulates (inhalable, respirable and < 300 nm), metals and VOCs emitted during the three phases of SLS, utilising nylon and alumide powders.

3 To assess the concentration of particulates (inhalable, respirable and < 300 nm), metals and VOCs that AM operators are exposed to, during the three phases of SLS, utilising nylon and alumide.

1.3 Hypothesis

Emission of particles, including submicron particles, and VOCs can take place from desktop FDM^{TM} printers, while utilising nylon filaments (Azimi *et al*., 2016; Stabile *et al.,* 2016; Kwon *et al*., 2017; Zhang *et al*., 2017).

1. Therefore, it can be hypothesised that HCSs (particulates, metals and VOCs) are emitted into the workplace atmosphere where SLS, utilising nylon and alumide powder, takes place.

Personal respiratory exposure to HCSs could possibly take place during AM, especially during physical contact with the powders (Graff *et al*., 2016). During the AM process, AM operators manually sieve powders, refill powder bins and manually remove the build and unsintered particles. These activities all involve direct contact with powders (Elliott and Love, 2016).

2. Therefore, it can be hypothesised that AM operators experience personal respiratory exposure to HCS (particulates, metals and VOCs) during SLS with nylon and alumide powder.

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CHAPTER 2: LITERATURE STUDY

This chapter includes a discussion of different elements of additive manufacturing (AM), relevant to this study. Although AM consists of various types of process categories, emphasis is placed on powder bed fusion (PBF). Selective laser sintering (SLS), a PBF technology and the three phases of this process, is summarised. The properties of different feedstock materials used during SLS, especially nylon and alumide, are described. The anatomy of the respiratory tract and the respiratory health implications of exposure to nylon and alumide are defined. The emission of hazardous chemical substances (HCSs) such as nylon and alumide particles, ultrafine particles (UFPs) and volatile organic compounds (VOCs) from AM is assessed. Different emission studies completed in the AM industry are discussed and relevant legislation regarding exposure to nylon and alumide and VOCs is explained.

2.1 Additive manufacturing (AM)

AM can be described as a process where feedstock is added layer by layer to create three-dimensional (3D) objects (Wohlers and Caffrey, 2015; ASTM, 2016; Rayna and Striukova, 2016). When comparing traditional methods of manufacturing to AM, the latter presents some important advantages. Complex geometries, which could not have been produced before, can now be created with AM, leading to a sense of designer freedom. Less harmful materials are used and the process of assembling parts to create objects is also eliminated, because fully functional objects can be created with AM (Ivanova *et al*., 2013).

Sheet lamination, direct energy deposition (DED), material jetting, material extrusion, binder jetting, powder bed fusion (PBF) and vat photopolymerisation are the seven standard AM process categories as classified by the American Society for Testing and Materials (ASTM) (Wohlers and Caffrey, 2015; ASTM, 2016). Sheet lamination, also known as laminated object manufacturing (LOM), creates 3D objects through cutting and bonding material sheets, DED is a process where materials are melted and fused using thermal energy as materials are being deposited. Creating 3D objects by using material jetting is possible, when a nozzle deposits droplets of materials. This is similar to material extrusion where a pressure system inside a nozzle is used to deposit materials for the build. Binder jetting is a process where a 3D object is created by powder materials bonded by a bonding liquid. A solid 3D object created by vat photopolymerisation results from a light source applied to the material, causing a chemical reaction called photopolymerisation in the materials (Gibson *et al*., 2015; Stucker, 2011; Wohlers and Caffrey, 2015). PBF is the AM process where powders are fused by thermal energy, created by an electron beam or laser (Wohlers and Caffrey, 2015; ASTM, 2016). Selective laser sintering (SLS), electron beam melting (EBM), direct metal laser sintering (DMLS) and selective laser melting (SLM) are some of the technologies of PBF (Wohlers and Caffrey, 2015).

The types of feedstock used in AM include solids, powders and liquids, each with its own set of properties and advantages functional for the production of AM parts (Short *et al.*, 2015). Different types of AM machines are used, including industrial sized machines that build objects meters in length or smaller desktop printers that are used to build smaller objects (Conner *et al*., 2014).

2.1.1 Powder bed fusion (PBF) and selective laser sintering (SLS)

PBF is an AM process category where powder is supplied to a powder bed and then fused by a thermal energy source (Wohlers and Caffrey, 2015; ASTM, 2016). There are three important elements needed in PBF systems: first a mechanical part which applies the layers of powder; second a fusion method to ensure efficient bonding of powder and last a thermal source, such as an electron beam or laser (Gibson *et al.*, 2015; Wohlers and Caffrey, 2015). A more detailed 3D object, with a higher quality of surface finish, can be expected when a PBF system uses a laser, while a faster build speed and fewer build support structures are associated with electron beam systems (Wohlers and Caffrey, 2015).

Four types of parameters are identified for PBF systems, viz. powder, scanning, temperature and laser related parameters. The laser parameters consist of the power provided by the laser as well as the frequency and pulse duration, while the shape, distribution and size of powders form part of the powder parameters. The scanning parameters include the pattern, spacing and speed of scanning. Uniformity of temperature and the powder bed temperature are collectively the temperature parameters that influence the build. To successfully fuse powders, the energy input should be efficient, determined by the temperature, scanning and laser parameters. During processing, the powder parameters influence the layering of powder on the powder bed and thermal conductivity. To be able to print a high quality product it is important to always ensure that the temperature of the powder bed is stable, as small deviations could cause distortion of parts (Gibson *et al.*, 2015).

SLS is a PBF technology where a CO_2 laser beam is used to fuse powder feedstock to form a 3D object (Wong and Hernandez, 2012). SLS has the potential to use both metals and plastics (Wohlers and Caffrey, 2015). During SLS powder materials are applied to a build area, followed by a roller mechanism used to smooth off the powder layer before sintering starts. Nitrogen gas is used inside the enclosed build chamber of the machine to limit powder degradation and oxidation. The type of powder utilised will determine the build chamber's temperature, which is always lower than the melt point of that specific powder. When the appropriate temperature in the chamber is reached and the roller has produced a smooth powder layer, the laser energy produced by the laser beam is absorbed by the powder material. A melt pool is formed when the powder is melted by the laser. Then the melt pool fuses the rest of the powder to connect the layers with each other (Gibson *et al.*, 2015; King *et al.*, 2014). After each layer has been completed, the powder bed will be lowered in the machine and a new powder layer will be applied and the process will be repeated. Depending on the feedstock, recycling of the unused powders is also possible (Wong and Hernandez, 2012).

2.1.2 The three phases of AM

AM involves three main phases, namely pre-processing, followed by processing and then the post-processing phase (Aubin, 1994).

The pre-processing phase can be split up into various steps which need to be completed before processing can take place. Firstly, a computer-aided design (CAD) model of the object is constructed (Aubin, 1994; Mahindru and Mahendru, 2013). After the CAD model has been completed, a stereolithography (STL) format is created from the CAD file. The STL format utilises planar triangles to represent the surface of the 3D image (Mahindru and Mahendru, 2013). During the pre-processing phase software parameter setup and physical setup takes place. During software parameter setup, the settings of the machine will be adapted for the specific build to be constructed and for the feedstock that will be used. As stated before, there are four parameters of importance for PBF, namely powder, scanning, temperature and laser related parameters (Gibson *et al.*, 2015). The physical setup follows, during which the AM operator prepares the AM machine. The build chamber is cleaned with a vacuum cleaner, powders are sieved and the powder bins of the AM machine are filled (Elliott and Love, 2016).

After the pre-processing phase has been completed, the processing phase (build phase) takes place (Aubin, 1994). During this phase, the build is monitored by the AM operator and therefore, interaction between the operator and AM machine is limited (Elliott and Love, 2016). During the processing phase of SLS, a metal plate, also called the table of the AM machine, is coated with a layer of polymer powder and is placed into the heated sintering chamber. The powder particles are fused by a CO_2 laser that emits the heat needed for melting the powder particles (Aubin, 1994; Scholten and Christoph, 2001; Wong and Hernandez, 2012). A new powder layer is added after the previous powder layer has been sintered. The object is formed after a predetermined amount of cycles are completed. The object is then held firmly in a block after the build is completed. The block needs to cool down before the built chamber is opened to remove the block (Scholten and Christoph, 2001).

Finally, during the post-processing phase which follows the processing phase, the block is removed and the object is separated from the block. (Aubin, 1994; Scholten and Christoph, 2001; Mahindru and Mahendru, 2013). Unsintered powders are removed from the printed object. The appearance and durability of the object could then be improved by surface treatments, such as painting, sanding or sealing (Deak, 1999; Scholten and Christoph, 2001; Mahindru and Mahendru, 2013). In order to re-use unsintered powders from previous builds, virgin (new) powders are combined with the used powders, because the mechanical and thermal properties of powders are altered when it is heated (Wohlers and Caffrey, 2015).

2.2 Feedstock used during SLS

The feedstock utilised during AM is available in powders, solids or liquids, and the physical form used is determined by the specific process (Short *et al.*, 2015). A variety of metal and plastic powder feedstock, such as nylon, alumide, stainless steel, silver or copper-based alloys can be used in SLS (Kruth *et al.*, 2003; De Beer *et al*., 2012; Wohlers and Caffrey, 2015). The types of powder used most frequently during SLS is polymer powders, such as polyamides (PA), polypropylene and polystyrene (Kruth *et al.*, 2003; Wohlers and Caffrey, 2015). Polymer feedstock can be divided into thermoset plastics or thermoplastics, depending on the properties and behaviour of the polymer feedstock when it is exposed to very high temperatures (Wohlers and Caffrey, 2015). Binder materials can be added to the powders when the sintering properties of the polymer powders are weak (Kruth *et al.*, 2003). The surface quality and the mechanical integrity of any object built with AM should meet certain expectations and requirements. These requirements are dependent not only on the process, but also on the feedstock utilised (Caulfield *et al.,* 2007).

In the following sections, nylon and alumide are discussed in more detail as they are relevant to this study.

2.2.1 Nylon

Nylon, one of the synthetic polyamides (plastic) powders often used during PBF, is classified as a thermoplastic indicating that it can be melted and cooled repeatedly without any of the feedstock properties being lost in the process (Chung *et al*. 2015; Wohlers and Caffrey, 2015). Different types of nylon, such as nylon-6, nylon-11 or nylon-12, can be utilised during SLS. Low friction, chemical resistance and high strength are some of the properties making nylon-6 suitable for use during SLS. Nylon-11 and nylon-12 contain the same type of properties and are almost clear in colour whereas nylon-6 is whiter (Tiwari and Pande, 2013).

2.2.2 Alumide

Hardness, strength and rigidity are some of the important properties required by feedstock used in AM. By combining different types of feedstock, these properties can be improved to ensure that a high quality product is delivered. Materials, such as carbon fibres and aluminium, are often mixed with nylon to improve the properties of the feedstock (Wohlers and Caffrey, 2015). Aluminium and nylon can be combined to create a compound called alumide, which is known as a metal-polymer and has various properties making it suitable for AM (Combrink *et al*., 2012; De Beer *et al*., 2012). These properties include high stiffness, good machinability and limited thermal conductivity (EOS, 2014).

The following section discusses the deposition and removal mechanisms of particles in the human respiratory system as well as factors, such as particle size, that can influence the area where particles are deposited.

2.3 Particulate deposition in the respiratory tract

After air is inhaled through the nose and mouth, it passes through the upper airways, which consist of the pharynx and larynx. Then it passes through the trachea into one of two bronchi, each leading into one of the lungs. The air then flows through the bronchioles to move into the alveolar sacs of the lungs, where gas exchange takes place (Widmaier *et al.,* 2016). Generally, humans inhale billions of particles daily and the charge, shape, density and size of these particles will largely determine the area of deposition (Heyder, 2004).

The three classes of particle size fractions that should be considered when workers are exposed to airborne particulate matter are inhalable, thoracic and respirable particle size fractions. The inhalable dust size fraction can be classified as a particle size having 50% penetration (cut-point) into the mouth and nose (aerodynamic diameter of up to 100 µm), while the thoracic dust size fraction is a particle size that have a 50% penetration (cut-point) into the upper regions of the bronchioles (aerodynamic diameter of up to 10 µm). The respirable dust size fraction is a particle size with a 50% penetration (cut-point) into the unciliated alveoli sacs (aerodynamic diameter of up to 4 µm) (CEN, 1993; Brown *et al.,* 2013).

Diffusion, inertial impaction, sedimentation, electrostatic attraction and interception represent the mechanisms by which inhaled particles deposit into the different areas of the respiratory tract (Heyder, 2004; Darquenne, 2012; Marano and Guadagnini, 2016). Diffusion, also known as random movement of particles, is the dominant deposition mechanism for particles with a diameter smaller than 100 nm. When the size of particles decreases, there is an increase in the distance that a particle can travel. The deposition of particles through inertial impaction takes place because of the inability of particles, mostly larger than 1 µm, to change direction when the airflow changes direction. This causes the particles to collide with the walls of the airways (Heyder, 2004; Darquenne, 2012). Particle deposition through inertial impaction is more effective for larger particles and when airflow, particle density and particle size, which increase the effectiveness of these mechanisms also increases (Heyder, 2004). Deposition of particles in the airway through sedimentation is caused by the effect that gravity has on the particles (Darquenne, 2012). The mechanism of sedimentation is effective when particle diameter is larger than 0.01 µm (100 nm) and with an increase in particle density and size, the effectiveness of this mechanisms also increases (Heyder, 2004). During interception particles collide with the walls of airways while moving along with the inhaled airstream. During electrostatic attraction charges are transferred to the walls of airways from charged particles in close proximity. Therefore, the respiratory walls are charged and particles with opposite charges are then attracted to the respiratory walls (Darquenne, 2012).

The respiratory system has certain mechanisms that eliminate particles entering the airways. The mucus found in the nose and mouth and the hairs in the nose are the first line of defence that captures particles before moving further into the airways. Mucus secretion by epithelial cells in the airways down to the bronchioles also captures particles in the inhaled air and the cilia found in this area transport the particle-laden mucus upwards through the airways to the throat from where it can be swallowed. If particles reach the alveoli, elimination by macrophages occurs. Macrophages are cells that destroy particles by engulfing them (Widmaier *et al.,* 2016). Particle solubility, size and chemical composition are some of the factors that affect the clearance of particles from the lungs (Marano and Guadagnini, 2016).

2.4 Particulate and VOC emissions during additive manufacturing

The following section evaluates all published emission studies of particulates and VOCs available from various process types of AM utilising different feedstock materials. Although these studies do not necessarily indicate emission during SLS utilising nylon and alumide, there are still similarities between the processes and feedstock used.

2.4.1 Particulate emissions during various process types of AM

UFPs and nanoparticles are two terms used alternatively to describe particles with a diameter of less than 100 nm (Oberdörster and Utell, 2002). Several studies have confirmed the emission of UFPs from fused deposition modelling (FDM^{TM}) printers. The main feedstock materials used in these studies were polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and nylon filaments or cartridges (Kim *et al.*, 2015; Azimi *et al*., 2016; Stabile *et al.,* 2016; Steinle, 2016; Yi *et al*., 2016; Zontek *et al.*, 2016; Kwon *et al*., 2017; Zhang *et al*., 2017). After the printing process has begun, there is an initial increase in the concentration of UFPs emitted, followed by a decrease in the concentration of UFPs as the printing process progresses (Kim *et al.*, 2015; Azimi *et al*., 2016; Kwon *et al*., 2017; Zhang *et al*., 2017). Yi *et al*. (2016) detected UFP emission from desktop 3D printers using real time instruments and Scanning Electron Microscopy (SEM), a technique where the material is observed in a 2D (two-dimensional) image, to indicate that UFPs were indeed emitted. During processing, a peak concentration of 3×10^{11} p/m^3 in the air was reached. After processing was completed, the concentration decreased again.

The printer model and type of feedstock utilised, together with environmental conditions and printing chamber temperature variations, could affect the emission of UFPs significantly (Kim *et al*., 2015; Azimi *et al.,* 2016; Stabile *et al.,* 2016; Steinle, 2016; Yi *et al*., 2016; Zontek *et al*., 2016; Kwon *et al*., 2017; Zhang *et al*., 2017). Azimi *et al*., 2016 measured particle emission while using different types of printers and feedstock materials. The study concluded that printers that utilised PLA filaments had the lower median emission rates (~ 10^8 p/min), compared to printers utilising ABS (~2×10^{10} to ~9×10^{10} p/min). Kim *et al.*, 2015 made similar conclusions following a study using two different FDM^{TM} printers (3DISON Plus, Rokit, Korea and Cube 3D Systems), utilising ABS and PLA cartridges. ABS had a higher emission rate of 1.61×10^{10} p/min, compared to PLA, which had an emission rate of $4{,}89 \times 10^8$ p/min. Because of higher emission rates and concentrations of particles released by ABS, it was concluded that PLA is less harmful than ABS. This study done by Kim *et al.*, 2015 also indicated that the emission rate did not differ significantly when the same type of feedstock was used in two different printers (PLA: 4.89×10^8 vs. 4.27×10^8 p/min). Steinle (2016) indicated that emissions rates were higher when printing occurred for shorter periods and when the objects being printed were lighter in weight. During this study, an emission rate of 2.1×10^9 p/min was detected when PLA was utilised, while 2.4×10^8 p/min was measured during ABS utilisation.

Yi *et al*., 2016 performed a study to determine if different colours of ABS and PLA filaments, such as blue, red and black, affect the size of particles being emitted. The authors reported that the smallest particles were emitted by black ABS and the largest particles by blue ABS. This conclusion indicated that the colour and type of filament used does affect the size of particles emitted.

Zhang *et al*. (2017) also investigated the effects of filament type, printer brand, filament brand and filament colour on the emission of particles, by placing focus on the use of ABS, PLA and nylon filaments in FDM^{TM} printers. The emission of particles while utilising ABS, was not significantly affected by the colour of the filament but was affected by the filament brand and printer brand used. The emission while utilising PLA, indicated that only the brand of printer used, caused observable variations. It was found during this study that some particles emitted by ABS and nylon were above 100 nm in size, while PLA only emitted particles smaller than 100 nm (Zhang *et al.,* 2017).

Zontek *et al.* (2016) found that the concentration of particles in the breathing zone of operators and inside the build chamber increased as the temperatures of the chamber increased during AM. Zontek *et al*. (2016) also compared the concentrations of particles in the breathing zone in a ventilated and unventilated room. A particle number concentration of 1 x 10^{10} p/m^3 was measured in the breathing zone while printing with ABS filaments in a non-ventilated room, while 3 x 10^9 p/m^3 was measured while utilising PLA in a well-ventilated room. Two other studies also reported that the ventilation in the room where printing occurred, influenced the concentration of UFPs in the printing rooms (Stephens *et al*., 2013; Steinle, 2016).

Recent studies sourced nylon filaments in FDM^{TM} printers not only to determine the emissions while using this type of feedstock, but also to compare the emissions to other types of feedstock. Several studies have detected the emission of particles, especially UFPs, from FDM^{TM} printers utilising nylon filaments (Azimi *et al*., 2016; Stabile *et al.,* 2016; Kwon *et al*., 2017; Zhang *et al*., 2017). Azimi *et al.* (2016) carried out a study where nylon filaments were utilised in a desktop FDM^{TM} printer, enclosed in a steel chamber. A condensation particle counter (CPC) was used to measure the concentration of the particles inside the chamber. At an extruder temperature of 230°C, nylon filaments released UFPs, with a median emission rate of 2 x 10^8 min^{-1} (Azimi *et al.,* 2016). Kwon *et al*. (2017) and Stabile *et al*. (2016) also indicated emission of UFPs during the use of nylon filaments. The study of Kwon *et al*. (2017) indicated that nylon is an overall high emitter of UFPs with particle number concentrations of 1.05 x 10^{11} to 4.34 x 10^{11} p/min at an extruder temperature of 265°C (>80% UFPs). Higher emission rates were visible in this study, when compared to the study by Azimi *et al.* (2016), because of higher extruder temperatures used (Kwon *et al*., 2017). The effects of different printing temperatures on particle emission were assessed by Stabile *et al.* (2016) and it was indicated that particle emission only occurs at temperatures above 230°C, while nylon is utilised.

Kwon *et al*. (2017), Stabile *et al*. (2016) and Zhang *et al.*, (2017) reported that during processing there was an increase in particle emission from nylon, followed by a decrease. The increase could be due to the increase in temperature, while the 3D printer is warming up. It was observed that the concentration of larger particles (> 100 nm) still increased after the concentration of UFPs decreased. This could be due to the time it takes for larger particles to develop and be emitted (Zhang *et al*., 2017).

The information above gives a clear indication of particle emission from FDM^{TM} printers while utilising nylon filaments. This possibly indicates that particle emission could take place from industrial 3D printers utilising nylon powders and so a study to investigate this possibility is justified.

2.4.2 VOC emissions

Azimi *et al.* (2016) and Steinle (2016) both concluded that the emission of VOCs takes place from desktop 3D printers utilising ABS, PLA and nylon filaments. In a study by Steinle (2016), VOC emissions from desktop 3D printers were reported during the use of ABS and PLA filaments. During the printing process, constant levels of VOC release was observed. The volatility of the constituents of the polymer and type of polymer used determined the type of VOC released, while the VOC concentration was influenced by the type of printer (Azimi *et al*., 2016; Steinle, 2016). PLA primarily emitted lactide, ABS emitted styrene, while caprolactam was primarily released from a nylon-based filament, namely plasticised copolyamide thermoplastic elastomer (PCTPE). For the nylon filament, the emission rate of caprolactam was 180 µg/min (Azimi *et al*., 2016). Wojtyla *et al.* (2017) performed a study where thermoplastics such as nylon, ABS and PLA filaments, were exposed to high temperatures to assess the VOC emissions. Cyclopentanone and propylene glycol were the VOCs emitted during the utilisation of nylon (Wojtyla *et al*., 2017).

Stefaniak *et al*. (2017) performed a study were VOC release was monitored while different colours of ABS and PLA filaments were utilised in a FDM^{TM} printer (MakerBot). The results indicated an overall lower total of VOC released for PLA filaments when compared to ABS filaments. When compared, the transparent blue PLA had an overall emission rate of 131 ug/h, while blue ABS had an emission rate of 2385 ug/h. Similar results were observed when using red ABS and red PLA (2383 *vs*. 49 ug/h). During individual VOC analysis, 13 types of VOCs were detected for ABS filaments, while nine different VOCs were detected for PLA filaments. Isopropyl alcohol, acetone, ethanol and acetaldehyde were the VOCs detected for both ABS and PLA filaments. Some colour influences were identified, for example the acetaldehyde concentrations were higher for red and blue ABS, when compared to the red and blue PLA. With other VOCs, such as ethanol, the colour of the filament did not influence the concentration of the VOCs (Stefaniak *et al.,* 2017). Stefaniak *et al*. (2017) concluded during this study that the type and colour of the filament could influence the emission of VOCs during AM.

The following section discusses the results of an emission study done during SLS. Although it does not make use of nylon and alumide, it gives a clear indication of what can be expected during this process technology.

2.5 Occupational exposure during SLS

Preparation of the AM machine, creation of software files, monitoring the build, post-processing and resetting of the machine are the responsibilities of the AM operator (Elliott and Love, 2016). During the preparation of the machine, the operator has to sieve powders and fill powder bins manually. Post-processing consists of de-powdering activities where unsintered powders are manually removed from the build (Elliott and Love, 2016). These activities lead to direct contact of the operator with the powders. Because powder feedstock is mostly used during SLS, and powders such as polycarbonates and nylon are light in weight, it could present possible respiratory health risks for AM operators (Kruth *et al.*, 2003; Short *et al.*, 2015).

Graff *et al.* (2016) established that occupational exposure to particles and UFPs takes place during AM. During this study an industrial 3D printer (EOSINT M270) utilising a metal alloy (IN939), containing nickel, chromium and cobalt, was used to analyse particle emission by using different measuring techniques, to sample different particle size fractions. Particle fractions of 10 to 300 nm were detected by nanotracers (NTs), while particle fractions of 300 nm to 10 µm were detected by a Lighthouse handheld 3016 IAQ instrument. In addition to the above mentioned methods, personal and area gravimetric sampling were also conducted. The NTs revealed that the floor contained a large amount of metal particles that settle soon after emission. When compared to background concentrations, a peak concentration of particles (16 000 p/cm^3), with sizes of 50 to 150 nm, was detected by the NTs, while the machine was cleaned. The study indicated that there is a limited amount of particle generation of particles smaller than 300nm. The Lighthouse instrument is capable of measuring various particles size fractions, such as 0.3, 0.5, 1, 2.5, 5 and 10 µm. The results indicated that homogenous emission of these particle sizes took place and increased levels were detected, while the metal powders were manually handled. The results of the Lighthouse instrument clearly indicate increased particle emission during activities such as vacuuming and handling the building plate inside the machine, metal powder streaming, machine cleaning and loading of metal powder into the machine. While the metal powder was strained and the machine cleaned, peaks of 3 x 10^7 p/m^3 were identified.

After gravimetric sampling was conducted, samples were analysed by Inductively Coupled Plasma Quadrupole-based Mass Spectrometry (ICP/QMS) to identify metals present in samples. The results indicated that during the 45 minutes of collecting the samples, the nickel, chromium and cobalt concentrations increased in the air. Additional laser diffraction analysis of the metal powder, both new and used, was performed which revealed size distribution differences (Graff *et al.*, 2016). Graff *et al.* (2016) indicated that exposure to and properties of particles would differ depending on the alloy composition and measuring instrument brand used.

2.6 Health effects

The following section provides an in-depth look at the adverse health effects associated with exposure to different forms of nylon, alumide, UFPs and VOCs. The routes of exposure to particulates and the health implications that follow are also explained.

2.6.1 Health effects associated with nylon exposure

A recent case study reported that exposure to nylon fibres during AM could lead to a rare type of pneumoconiosis, known as nylon flock worker's lung. In this case a worker was exposed to nylon fibres during SLS and experienced fever, coughing and chills (Johannes *et al*., 2016).

2.6.2 Health effects associated with aluminium exposure

Aluminium is a well-known neurotoxicant that can be absorbed into the body following inhalation, ingestion or dermal exposure (Yokol and McNamara, 2001; Kawahara *et al*., 2007). It was found that the absorption of aluminium through the lungs is far more efficient than absorption through the gastrointestinal tract (Yokol and McNamara, 2001). When aluminium attaches to DNA, it can influence protein transcription, which is necessary for the protein-DNA structure to be synthesised and broken down (Lukiw *et al.,* 1998). Parkinson's disease, multiple sclerosis, dementia and cognitive deficiency are neurodegenerative diseases associated with aluminium exposure (Kawahara *et al*., 2007; Exley, 2014).

Symptoms such as coughing and shortness of breath were found during a case study of a man working in a firework factory for ten years. These symptoms were connected to his exposure to aluminium powder. Formation of cholesterol granulomata and pulmonary fibrosis were identified in his medical examinations (Rodrigo *et al.,* 2015). An undeviating relationship has been reported to exist between aluminium industry workers with pulmonary fibrosis and their respiratory exposure to aluminium powders (Krewski *et al*., 2007). Following a study conducted with gold miners from Western Australia, Peters *et al*. (2013) reported that there is a possible connection between Alzheimer's disease and exposure to aluminium dust.

2.6.3 Health effects associated with exposure to UFPs

It was already indicated that AM utilising nylon could lead to the emission of UFPs into the air (Kwon *et al*., 2017; Stabile *et al*., 2016). The respiratory and oral pathways are two main routes of entry for UFPs into the body and the interaction between human and UFPs is dependent on a variety of characteristics, such as shape, roughness, composition, size and charge of particles (Hoet *et al*., 2004; Elsaesser and Howard, 2012). A study which compared the health effects of coarse and fine particles with UFPs, found that all the particles lead to the generation of reactive oxygen species (ROS) and therefore oxidative stress, but the degree of the oxidative stress was increased with UFPs (Li *et al*., 2003). Alteration of biological membranes, lipids and DNA may result, because of the oxidative stress caused by the ROS that develop following UFP exposure (Marano and Guadagnini, 2016). Once UFPs are inhaled and deposited into the lungs, the alveolar macrophages phagocytise the UFPs which then move into the alveolar interstitium. From there it passes to the lymphatic ganglions and then it is transferred into the blood stream. Impaired lung function, airway inflammation and fibrosis of the lung tissue may develop when clearing mechanisms do not eliminate the UFPs from the lungs (Marano and Guadagnini, 2016; Viitanen *et al.,* 2017). After respiratory exposure to submicron particles it will penetrate to the alveoli and into the blood circulation and it has been identified that alveolar cells exposed to submicron particles undergoes a change in structure and function, because of damage to cell organelles (Mazzarella *et al.,* 2014; Izhar *et al*., 2016). Zhu *et al.* (2008) identified respiratory exposure of rats to submicron particle lead to oxidative stress and acute lung damage.

Nemmar *et al.* (2001) indicated that cardiac function and homeostasis could possibly be affected by UFPs, after a study that has been completed on animals indicated diffusion of UFPs into the systemic circulation from the lungs. Stefaniak *et al.* (2017) reported that the mean arterial pressure in rats was notably elevated after respiratory exposure to particle emission, with a mean aerodynamic diameter of 70 nm, from a desktop 3D printer. Systemic microvascular dysfunction followed the elevation of the mean arterial pressure. Fang *et al*., (2010) reported that there is a strong association between the development of ischemic heart disease, systemic inflammation and heart rate variability, and exposure to particulate matter. Marano and Guadagnini (2016) indicated that there is a possibility that endothelial dysfunction could arise due to UFP exposure and that could cause myocardial infarctions or atherosclerosis.

UFP exposure can also lead to physical damage, protein misfolding and membrane perturbation after entering the body (Elsaesser and Howard, 2012). Animal studies indicated the presence of UFPs in the central nervous system (CNS) after being inhaled (Oberdörster *et al.,* 2004). Most of the research done on the effects of UFPs on the body, is obtained through animal studies and cannot always be used to indicate the effects that the UFPs will have on humans (Marano and Guadagnini, 2016).

2.6.4 Adverse health effects associated with VOCs

Various illnesses have been associated with exposure to both inorganic and organic air pollutants. Organic air pollutants could lead to the development of visual disorders, dizziness, memory disorders, headaches and irritation. Both animals and humans are susceptible to the development of cancer when exposed to specific types of VOCs, such as benzene, chloroform and formaldehyde (Snyder, 2000; Guo *et al.,* 2004; Zhang *et al.,* 2008; Wojtyla and Baran., 2015). The VOC, acetone, could cause health effects, such as eye irritation and nasal pungency at very high concentrations (10 000 – 40 000 ppm), while other VOCs, such as naphtha, have been associated with respiratory system impairment (Arts *et al*., 2006; Zailina *et al*., 2009). The hazardous substances data bank (Cited by Kim *et al.,* 2012) indicated that pentane exposure could cause confusion, dizziness and respiratory arrest. However, during the study completed by Kim *et al*. (2012) where rats were exposed to pentane, no toxic effects were determined. Another literature study has also indicated that n-pentane did not cause any adverse health effects, such as respiratory or eye irritation, mutagenicity or genotoxicity (EU, 2003).

As discussed previously, caprolactam, cyclopentanone and propelyne glycol are the VOCs that have been detected during 3D printing that utilised nylon (Azimi *et al*., 2016; Wojtyla *et al*., 2017). Irritation and dryness of the throat and the ocular system are symptoms that have been experienced by test subjects exposed to propylene glycol mist (Wieslander *et al*., 2001). Ziegler *et al*. (2008) conducted a study where test subjects were exposed to ε-caprolactam to investigate possible irritation symptoms, but most results were not statistically significant. However, it was noted that concentrations of 5 mg/m^3 caused irritation of the nasal mucous membrane.

2.7 Occupational exposure limits for nylon and alumide

There is no occupational exposure limit (OEL) for exposure to nylon in South African or international legislation. An occupational exposure limit (OEL) is the upper limit of a concentration that an employee could be exposed to, which should not be exceeded. Due to no national or international OEL for nylon, the exposure results of AM operators to nylon will be compared to the OELs of total inhalable and respirable dust that have been assigned OELs as indicated in Paragraph 36 of Annexure 1 of the Hazardous Chemical Substances Regulations (HCSR) (HCSR, 1995). The Time-Weighted Average Occupational Exposure Limit – Recommended Limit (TWA-OEL-RL) for total inhalable dust over an eight-hour work shift is 10 mg/m^3 and for respirable dust 5 mg/m^3. Even though the respiratory exposure samples for nylon cannot be analysed specifically for nylon, it can be assumed that the majority of dust that the AM operators are exposed to is nylon and therefore in this study the term “nylon dust” will be used to describe the exposure of AM operators during SLS utilising nylon. During SLS with alumide the term “alumide dust” will be used, because operators are exposed to alumide powder which is a combination of nylon and aluminium. The aluminium fraction that the operators are exposed to will be compared to the TWA OEL-RL listed for aluminium in Table 2 of the HCSR. The TWA OEL-RL for aluminium is 10 mg/m^3 as a total inhalable dust and 5 mg/m^3 as a respirable dust (HCSR, 1995). The above inhalable aluminium dust OEL, over an 8-hour shift, equals the Workplace Exposure Limit (WEL) set by the Health and Safety Executive (HSE), while the respirable WEL is slightly lower, at 4 mg/m^3 (HSE, 2011). The Occupational Safety and Health Administration (1993) has set a Permissible Exposure Limit (PEL), over an 8-hour shift, of 15 mg/m^3 for inhalable aluminium dust and 5 mg/m^3 for respirable aluminium dust.

2.8 Conclusion

SLS is one of the technologies often used during PBF and can utilise both nylon and alumide as feedstock. The above mentioned literature studies indicate the emission of HCSs (particulates, metals and VOCs) during AM, which could lead to exposure of AM operators, resulting in the possible development of adverse health effects. It can be concluded that there is a need to determine the emission of and exposure to HCSs during the three phases of AM, utilising nylon and alumide, to be able to determine if AM operators are exposed. This can contribute to implement possible control measures and improve working conditions of AM operators.

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CHAPTER 3: ARTICLE

3.1 Guidelines for authors

Annals of work exposures and health

1. Annals of Work Exposures and Health publishes original research and development material that helps reduce risk of ill-health resulting from work and welcomes submissions in these areas.
2. *Originality:* Original research papers are reports of scientific investigations of matters affecting occupational risks, exposures, and methods of their assessment. Original research reports may be descriptive, observational and/or experimental investigations, and can usually be presented as hypothesis-driven research. Original research reports should be able to clearly state their aim, define the methods with which evidence is gathered and organized, describe the analytic methods used, and present the results of these analyses in a transparent and interpretable format. The conclusions of the paper must be supported by the data and their analysis. Original research papers are normally under 4000 words with a maximum of 5000 and have up to six tables or figures. Original research papers are peer reviewed through our normal process.
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This article contains more words than is permitted by the journal. This was done for examination purposes only. Especially for the methodology, more words were used to ensure that the methods of sampling are understood correctly. The discussion is also longer to ensure that all results and their potential meaning are clearly discussed. However, at actual submission of the manuscript, the maximum word count will be adhered to.

Respiratory exposure to hazardous chemical substances during additive manufacturing using nylon and alumide

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Abstract

Background: It is possible that hazardous chemical substances (HCSs) [particulates, metals and volatile organic compounds (VOCs)] are emitted during the three phases of additive manufacturing (AM), which could lead to the development of adverse health effects when the AM operators are exposed. Very little information is available regarding the area emission of and personal exposure to HCSs that should be expected during selective laser sintering (SLS), utilising nylon and alumide.

Aims: To assess the respiratory exposure to HCSs (particulates, metals and VOCs) experienced by AM operators during selective laser sintering (SLS), utilising nylon and alumide.

Methodology: Particle size distribution (PSD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF) analyses were conducted on both virgin (new) and used nylon-12 (PA2200) and alumide powders. Particle counters were used to determine the area emission of submicron particle number concentrations into the workplace. National Institute for Occupational Safety and Health (NIOSH) Methods 0500 and 7300 were used to determine the area emission of and personal exposure to inhalable and respirable sized nylon and alumide dust. Personal Nanoparticle Respiratory Deposition (NRD) samplers were used to determine the personal exposure of AM operators to particles < 300 nm and TraceAir personal VOC badges were used to determine the area emission of and personal exposure to VOCs during the three phases of AM.

Results: PSD results indicated that virgin and used nylon and alumide powders fell into the inhalable particle size range (63.85 – 65.30 µm). A difference was found between the measured volume weighted mean and the supplied information in the material data sheet (MDS), for both nylon and alumide powders. Results from the particle counters indicated an increase in particle number concentrations during all three phases of AM, when compared to ambient readings. Airborne particle counter (APC) results indicated the highest emission of the 0.30 µm particle size fractions. When personal exposure was monitored, the highest mean concentrations of exposure to inhalable and respirable sized nylon (5.52 mg/m^3 and 0.18 mg/m^3) and alumide (5.32 mg/m^3 and 0.59 mg/m^3) dust were during post-processing. Aluminium (Al), iron (Fe), titanium (Ti) and zinc (Zn) were the metals detected in area and personal exposure samples during SLS with alumide which could be cross-contamination from other AM processes. Acetone, pentane, toluene, chloroform and naphthas were the VOCs detected during SLS utilising nylon and alumide.

Conclusion:

SLS, while utilising nylon and alumide, resulted in area emission and personal exposure to HCSs (particulates, metals and VOCs). Area emission results indicated an increase in submicron particle number concentrations during all three phases of AM. Personal exposure during SLS utilising nylon and alumide indicated exposure to particulates during the post-processing phase, because of activities, such as removal and cleaning of builds. All VOC concentrations detected were low and personal exposure was below OELs.

Keywords: Nylon-12, PA2200, alumide, selective laser sintering, particle size fraction, hazardous chemical substances, area emission, personal exposure.

1. Introduction

Additive Manufacturing (AM), also known as three dimensional (3D) printing or rapid prototyping, is a process were 3D objects are built with material that is joined using printer technology (Wohlers and Caffrey, 2015; ASTM, 2016). AM has become a reliable manufacturing method, because of the cost reduction and quality of the products that are delivered. Therefore, aerospace, automotive and biomedical industries are all progressively making use of AM (Campbell *et al*., 2012; Guo and Leu, 2013; Wohlers and Caffrey, 2015). When comparing traditional methods of manufacturing to AM, it becomes clear that AM holds more advantages. Complex geometries, previously not possible, can be built by making use of AM and the assembly of parts to create objects is also eliminated because fully functional parts are delivered (Ivanova *et al*., 2013).

Sheet lamination, direct energy deposition, material jetting, material extrusion, binder jetting, powder bed fusion (PBF) and vat photopolymerisation are the seven process categories of AM (Wohlers and Caffrey, 2015; ASTM, 2016). PBF is an AM process category where powder feedstock is melted by thermal energy provided by an electron beam or a laser and thereafter the powder is cooled to form a solid object. The three important elements of a PBF system are: a mechanism which applies the powders to the powder bed, a bonding method to bind powders to one another and lastly a thermal source, such as a carbon dioxide (CO_2) laser or electron beam (Gibson *et al*., 2015; Wohlers and Caffrey, 2015). Electron beam melting (EBM), selective laser melting (SLM) and selective laser sintering (SLS) are technologies used in PBF. SLS, which is the focus of this study, is a technology where a CO_2 laser is used to fuse powder feedstock to create a 3D object (Wong and Hernandez, 2012; Wohlers and Caffrey, 2015).

Solid sheets, filaments, powders and liquids are the different forms of feedstock that can be utilised during AM and the type of feedstock used is dependent on the specific AM process (Guo and Leu, 2013). Plastics and metals can be utilised during SLS, provided that it is in a powder form (Kruth *et al.*, 2003; Wohlers and Caffrey, 2015). Polymer (plastic) powders, such as polyamides (PA), which consist of carbon to carbon bonds, are most commonly used during SLS (Gibson and Shi, 1997; Chung *et al*., 2015; Wohlers and Caffrey, 2015). Nylon, which is a synthetic PA, is often used during PBF and is classified as a thermoplastic. Thermoplastic feedstock can be melted and cooled continuously without any material properties being lost (Wohlers and Caffrey, 2015). Nylon-6, nylon-11 and nylon-12 are different types of nylon utilised during SLS (Tiwari and Pande, 2013). The properties of the feedstock used during AM can also be improved by combining different types of feedstock, such as nylon with aluminium, carbon fibres or glass (Wohlers and Caffrey, 2015). A combination of aluminium and polyamide powders is called alumide, which is a compound with extreme stiffness, limited thermal conductivity and high temperature performance (De Beer *et al*., 2012; EOS, 2014).

AM consists of three main phases, namely pre-processing, processing and post-processing (Aubin, 1994). During the pre-processing phase, a computer aided design (CAD) is created of the object being built, and thereafter a stereolithography (STL) format is created, which uses planar triangles to specify the surface of the 3D image (Mahindru and Mahendru, 2013). The preparation of the file, cleaning the machine, sieving the powder and filling the powder bins form part of the pre-processing phase (Elliott and Love, 2016). The processing phase follows, during which a metal plate is covered with polymer powder and then automatically lowered into a sintering chamber as the part is built. The powder particles are fused by a CO_2 laser that provides enough heat to melt the particles. A new powder layer is then applied after the sintering of the previous layer has been completed. After a predetermined number of cycles have been completed, the object built is enclosed in a solid block (Aubin, 1994; Scholten and Christoph, 2001; Wong and Hernandez, 2012). The object is then cooled, followed by the post-processing phase. This phase includes activities such as removing the object from the build chamber, removing excess powders, sanding and painting of the printed object (Aubin, 1994; Deak, 1999; Scholten and Christoph, 2001). Since the heat applied during the AM process alters the mechanical and thermal properties of the used powder, unsintered powders from the previous build are mixed with virgin powder (new or unused) in order to be reused (Wohlers and Caffrey, 2015). AM operators are directly exposed to AM powders during the manual handling of powders during pre-processing and post-processing activities (Elliott and Love, 2016; Graff *et al*., 2016). Graff *et al*. (2016) reported particle emission during metal PBF, specifically < 0.3 µm, during activities that included handling of the metal plate, machine cleaning and loading, powder streaming and vacuuming. During the processing phase the interaction of the AM operator with the AM machine is limited and his only responsibility is to monitor the build (Elliott and Love, 2016).

Numerous studies have indicated that particles, especially submicron particles, and VOCs are emitted from desktop fused deposition modelling (FDM^{TM}) printers. The feedstock from which emissions took place during these studies, were mostly polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) filaments or cartridges and nylon filaments (Kim *et al.,* 2015; Azimi *et al*., 2016; Stabile *et al*., 2016; Steinle, 2016; Yi *et al*., 2016; Zontek *et al*., 2016; Kwon *et al.,* 2017; Wojtyla *et al*., 2017; Zhang *et al*., 2017). Some studies have focussed on particle and VOC emission that take place during AM, when utilising nylon filaments and have also compared these to emissions from other types of feedstock (Azimi *et al*., 2016; Stabile *et al*., 2016; Kwon *et al.,* 2017; Zhang *et al*., 2017). Kwon *et al*. (2017) indicated that nylon is an overall high emitter of UFPs with particle number concentrations of 1.05×10^{11} to 4.34×10^{11} p/min at an extruder temperature of 265°C. With the onset of the printing phase, an increase in particle emission was observed, followed by a decrease after a peak was reached (Azimi *et al.*, 2016, Kwon *et al.*, 2017). Wojtyla *et al*. (2017) indicated that VOCs, such as cyclopentanone and propylene glycol, are released when nylon filaments are heated to 390 °C. Azimi *et al*. (2016) indicated that caprolactam, a monomer of nylon-6, is the primary VOC released during 3D printing utilising a nylon-based filament, namely plasticised copolyamide thermoplastic elastomer (PCTPE) (Thomas and Raja, 2005; Lithner *et al.,* 2011).

From the mentioned literature it can be deduced that AM operators could be exposed to nylon and alumide particles (including submicron sized particles) and therefore, possible adverse health effects should be considered. A recent study found that exposure to nylon fibres in the AM industry leads to a type of hypersensitivity pneumoconiosis, known as nylon flock worker's lung (Johannes *et al*., 2016). Aluminium is a neurotoxicant and exposure is associated with dementia, cognitive deficiency, Parkinson's disease and multiple sclerosis (Kawahara *et al*. 2007; Exley, 2014). Fang *et al*. (2010) reported that there is a correlation between the exposure to particulate matter and the development of diseases, such as systemic inflammation, ischemic heart disease and heart rate variations. Zhu *et al.* (2008) reported that respiratory exposure of rats to submicron particle lead to oxidative stress and acute lung damage.

AM operators are responsible for preparing and cleaning the machine, sieving powders, monitoring the build, removing the build, removing excess powder as well as sanding and grinding of the build (Elliott and Love, 2016). Numerous studies have confirmed the emission of hazardous chemical substances (HCSs) (particulates and VOCs) from FDM^{TM} printers using nylon-6 as feedstock, while there is no information available regarding the emission that results from the operation of industrial AM machines using nylon-12 (PA2200) and alumide powders. Previous studies also focused on the area emission of HCSs and not on the personal exposure of AM operators to HCSs. It is therefore undecided as to what concentrations of HCSs AM operators may be exposed to during the use of nylon-12 and alumide powders with SLS.

The aim of this study was firstly to determine the physical and chemical characteristics of virgin and used nylon-12 (PA2200) and alumide powders. Secondly, to monitor the emissions and respiratory exposure experienced by AM operators to HCSs (particulates, metals and VOCs) during SLS, utilising nylon-12 and alumide powders, at two AM facilities in South Africa. Because there is no national or international occupational exposure limits (OELs) for nylon, the exposure of AM operators to nylon was compared to total inhalable dust concentration (10 mg/m^3) and respirable dust (5 mg/m^3) that have been assigned OELs as indicated in the Hazardous Chemical Substances Regulations (HCSR) (HCSR, 1995). Although the personal respiratory exposure samples for nylon cannot be analysed, it is assumed that the majority of the airborne dust that operators are exposed to consists of nylon-12 (PA2200) particles. Therefore, for the purpose of this study the term "nylon dust" will be used to describe the airborne dust that operators are exposed to during the SLS with nylon-12 powder. During SLS with alumide, AM operators are exposed to a mixture of nylon-12 and aluminium airborne particulates and the term "alumide dust" will be used to describe these airborne particles. The operator's personal exposure is compared to the OEL for total inhalable dust (10 mg/m^3) and respirable dust (5 mg/m^3) and the aluminium fraction will be compared to the TWA OEL-RL listed for aluminium in the HCSR (10 mg/m^3 as a total inhalable dust and 5 mg/m^3 as a respirable dust) (HCSR, 1995).

2. Materials and Methods

2.1 Workplace description

The areas where SLS were performed showed distinguishable differences at the two AM facilities. At Facility A, the machines used for SLS (Formiga P110 and Formiga P100 from EOS, Munich, Germany), were located inside an enclosed room along with other types of AM machines. This facility made use of air-conditioning (HVAC) systems to ventilate the area where printing took place. The area where printing took place was adjacent to two other rooms, one where powder sieving and mixing took place and the other where compressed air was used for post-processing tasks. At Facility B, the machines used for SLS (EOSINT P 385 and EOSINT P 380 from EOS, Munich, Germany), were located inside the same room, but were separate from other AM processes. Adjacent to the printing area was a room where powder sieving, mixing and post-processing tasks were performed. Additionally, there was a deficiency of natural and mechanical ventilation at Facility B, which lead to the printing areas not being ventilated efficiently. At Facility A, only nylon was utilised, while at Facility B nylon and alumide were utilised.

2.2 Participants

This study included three AM operators from two AM facilities in South Africa who were experienced in SLS, utilising nylon and alumide.

Ethics approval for this study was obtained from the Health Research Ethics Committee of the North-West University (NWU-00010-17-S1).

2.3 Process description

During the pre-processing phase (facility A and B), the SLS machine was cleaned by using a vacuum cleaner, while the lens of the laser was cleaned with ethanol. Used powders were sieved, followed by the mixing of virgin and used powders by manually pouring virgin and used powders into the powder bin. The first part of pre-processing when the machine was cleaned, took place in the printing room, while the second part, when powders were mixed, took place in the adjacent room. The powder bins were then placed inside the AM machine. The last part of the pre-processing phase comprised of the loading of the print job (CAD file) and ensuring all settings were correct according to the print job's requirements. During the processing phase the AM machine was closed and the warm up of the machine initiated, which was followed by the building process (processing). After the build process had been completed, the object built had to cool down before it could be removed from the AM machine's sintering (build) chamber. During the post-processing phase, the machine was opened by the AM operator and a block consisting of loose powders surrounding the built part was removed. At Facility A, the area where most excess powders are removed is in the printing room, while at Facility B the build was manually moved to an adjacent room by the AM operator where the excess powder was removed with a brush. After the loose powder had been removed, compressed air was used to remove all particles from the object, inside a fully enclosed chamber with a local extraction ventilation (LEV) system. A brush was again used to ensure that no loose particles were left behind, followed by wiping the object with a cloth. The area where post-processing took place was afterwards cleaned with a vacuum cleaner. At both facilities, AM operators wore nitrile gloves, steel-toe shoes, a respirator and a laboratory coat. At Facility A, a dust mask (FFP2) with an active carbon moulded respirator was used, while at Facility B, a full-face respirator with a combination filter (organic gases and vapours, inorganic gasses and vapours, sulphur dioxide and particle matter) was used.

2.4 Physiochemical characterisation of feedstock

Samples of virgin and used powders, accompanied by material data sheets (MDSs), were collected from both facilities to determine and compare the physical characteristics (shape and size) of both nylon-12 (PA 2200) and alumide powders. Storage vials (50 ml with screw caps) (Environmental Express, South Carolina, USA) were used to collect and store the virgin and used powders, which were collected before pre-processing and after post-processing, respectively. Particle size distribution (PSD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF) analysis were used to determine the physical and chemical characteristics of powders.

PSD analysis was performed with the Malvern Matersizer 2000 particle size analyser (Malvern instruments, Malvern, United Kingdom) and version 5.31 software. According to manufacturer specifications the analysis took place by adding the powder to 100 ml ethanol, to ensure even dispersion of powder particles during analysis. Background measurements were taken, where after two samples of each powder were analysed three times.

SEM was used to produce two dimensional images of powders to be able to determine the size and shape of nylon (PA 2200) and alumide powders. This involved applying carbon tape to a sample stub, followed by powder application to the tape. The stub was then placed into a sputter holder, where it was coated with a gold palladium alloy. The specimen was then placed into a Phenom pro-desktop SEM (Phenom-world B., Eindhoven, Netherland) microscope for analysis.

XRF analysis was conducted on the nylon and alumide powders to determine their chemical composition. An Axios^{Max} machine was used to perform this analysis against OMNIAN standards (PANalytical, Almelo, Netherland). Pressed pellets were created, by adding a binding material to the powders and then these pellets were pressed under a weight of 20 tonnes. X-rays generated by X-ray tubes then scanned the samples to provide information on the chemical composition of the powder.

2.5 Area emission monitoring

A TSI Model 3007 Condensation Particle Counter (CPC) (TSI Inc., Shoreview, Minnesota, USA) and a TSI AeroTrak^{TM} Airborne Particle Counter (APC) (TSI Inc., Shoreview, Minnesota, USA) were placed in the area where the AM operator was working (1.5 m from floor and 1 m away from the source) and the particle number concentrations were recorded during the three phases of AM (pre-processing, processing and post-processing). The CPC measured the number concentrations of the particles with sizes of 0.01 µm to > 1 µm in the air and the APC measured the number concentrations of various particle size fractions (0.30 - 10.00 µm). Ambient readings were taken in the hall (1.5 m from the floor), outside the area where the AM printers were located for a period of 10 minutes. Due to instrument availability, only one sample was collected for each AM phase (pre-processing, processing and post-processing) and the particle number concentrations for the various AM phases shown in Figure 2 were not collected during the same build. Therefore, particle emissions were recorded with the APC and CPC, but these recordings and the personal exposure monitoring took place during the construction of different builds.

The National Institute for Occupational Safety and Health (NIOSH) Methods 0500 (particles not otherwise specified, total) (NIOSH, 1994) and 7300 [Elements by Inductively coupled plasma (ICP)] (NIOSH, 2003) were used to establish the emitted inhalable and respirable sized nylon and alumide dust in the atmosphere, during the three phases of AM. Area emissions of inhalable and respirable sized dust were measured by placing a Gillian Gilair Plus sampling pump (Sensidyne, Clearwater, Florida, USA) which was calibrated to a flow rate of 2 L/min and connected to a Institute of Occupational Medicine (IOM) sampler (SKC, Eighty Four, Pennsylvania, USA) in the immediate vicinity where the AM operator performed his duties (1.5 m from floor and 1 m away from operator) and sampling was done for the entire work shift, which included the three AM phases. The sampler was fitted with a mixed cellulose ester (MCE, 37 mm) filter (SKC, Eighty-Four, Pennsylvania, USA) and a multidust foam disc.

A TraceAir personal VOC badge (Assay Technology, Livermore, California, USA) was also placed in the area where the AM operator performed his duties and was replaced before each new phase, to be able to compare the VOC emissions of the three phases of AM. The printing rooms were large areas with adequate airflow, therefore, passive VOC sampling badges were deemed appropriate sampling media.

2.6 Personal respiratory exposure monitoring

Personal respiratory exposure monitoring of inhalable and respirable sized dust as well as particles < 300 nm were conducted simultaneously during the entire shift. NIOSH Methods 0500 (NIOSH, 1994) and 7300 (NIOSH, 2003) were used to determine exposure to inhalable and respirable sized nylon and alumide dust. A Gilian Gilair Plus sampling pump (Sensidyne, Clearwater, Florida, USA) was calibrated to a flow rate of 2 L/min and then connected to an IOM sampler (SKC, Eighty-Four, Pennsylvania, USA). The IOM sampler was fitted with a MCE (37 mm) filter (SKC, Eighty-Four, Pennsylvania, USA) and MultiDust Foam inserts and was placed in the breathing zone of the AM operator. The IOM sampler and pump was replaced prior to each phase.

For exposure to particles < 300 nm a second Gilian Gilair Plus sampling pump was calibrated to a flow rate of 2.5 L/min and then connected to a Personal NRD sampler (Zefon International Inc., Ocala, Florida, USA), which was also placed in the breathing zone of the AM operator for the entire shift. While sampling with a NRD sampler, the air enters through the aluminium cyclone (25 mm) that removes particles > 4 µm, followed by the transportation of respirable sized particles to the impaction part of the NRD sampler, where particles > 300 nm are removed. Particles < 300 nm are collected on eight nylon mesh screens (Cena *et al.,* 2011).

A TraceAir personal VOC badge (Assay Technology, Livermore, California, USA) was placed in the breathing zone of the AM operator to determine the concentration of VOCs that the AM operators were exposed to during each phase.

The gravimetric monitoring and VOC sample analyses (area and personal) were performed using standardised methodologies as published by NIOSH and analysed by a South African National Accreditation System (SANAS) accredited laboratory. Gravimetric analyses of both nylon and alumide samples were conducted to determine the total concentration of inhalable and respirable sized dust on the filter/multifoam disc, followed by Inductively Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES) analysis of all samples that were collected during SLS with alumide to determine the mass of aluminium present in the sample.

2.7 Statistical analysis of results

Basic descriptive statistics [mean, maximum, minimum and standard deviation (SD)] were primarily used to describe the results. Since the number of available operators was limited to three and a small number of prints could be sampled, the personal exposure of operators was primarily described using descriptive statistics. Therefore, the results from the study will be used as an initial indication of the range of concentrations that operators are exposed to during SLS with nylon and alumide. Independent t-tests were used to determine the particle sizes of virgin and used nylon and alumide powders so that any statistical significant differences can be detected. Throughout a p-value ≤ 0.05 was considered as statistically significant. During the calculation of the means of each phase, as well as during the calculation of the time weighted average (TWA), the values below the detection limit (BDL) were assigned a value, calculated by dividing the detection limit (DL) by the square root of two. To determine the area emission of inhalable and respirable sized particles, the averages of all samples were determined. With concentrations of personal exposure to inhalable and respirable particles the TWA was calculated using the average concentrations of all samples for each phase and the average duration of all samples for each phase. For the area and personal VOC calculations, the TWA of each sample was calculated, by using the concentration of the VOC measured during each phase and the duration of each measurement.

3. Results

In the following section, the data of the PSD, SEM and XRF analyses of virgin and used powders from both facilities are provided, followed by area emission of HCSs (particulates, metals and VOCs) and personal exposure to HCSs (particulates, metals and VOCs) during the three phases of AM.

3.1 PSD, SEM and XRF analysis

The volume weighted mean particle size of nylon powder ranged between 64.99 ± 0.21 µm for virgin powder to 65.30 ± 0.68 µm for used powder at Facility A and B (Table 1). This was approximately 9 µm larger than the powder size indicated on the MDS of the virgin powder used at Facility A and Facility B. Fraction specific size comparisons [d(0.1), d(0.5) and d(0.9)] showed significant differences between the particle sizes of virgin and used nylon powders at Facility A while no significant difference was found for the volume weighted mean sizes. A significant difference was found in d(0.1) particle sizes of virgin and used nylon powder at Facility B while no significant difference was found for the volume weighted mean sizes. The mean virgin alumide particle size was approximately 4 µm larger than the particle size indicated on the MDS from Facility A. No differences in particle size and shape were observed between virgin and used nylon, according to SEM images (Figure 1 (a)-(d)). The SEM images (Figure 1) of alumide powder confirmed particle sizes of up to > 60 µm.

Table 1: PSD of virgin and used nylon (PA 2200) and alumide powder from Facility A and B.

Powder	**Facility**	**Type**	**MDS Mean**	**n**	**Particle size (µm)**			
					Volume Weighted Mean	**d (0.1)**	**d (0.5)**	**d (0.9)**
Nylon (PA 2200)	A	Virgin	56	6	65.08 ± 0.10	41.02 ± 0.87^{a}	61.95 ± 0.23^{b}	93.39 ± 1.41^{c}
		Used	-	6	65.30 ± 0.68	38.52 ± 0.42^{a}	61.22 ± 0.39^{b}	97.69 ± 2.29^{c}
	B	Virgin	56	6	64.99 ± 0.21	40.55 ± 0.54^{d}	61.76 ± 0.13	93.86 ± 1.17
		Used	-	6	64.84 ± 0.46	41.46 ± 0.26^{d}	61.92 ± 0.45	92.15 ± 0.70
Alumide	A	Virgin	60	6	63.85 ± 1.28	38.33 ± 0.49	60.23 ± 1.07	94.40 ± 2.93
	B	Used	-	6	64.35 ± 0.44	38.98 ± 0.55	60.80 ± 0.24	94.66 ± 1.73

MDS - material data sheet; n – number of samples; d(0.1) – 10% of the sample's particles are smaller than this diameter; d(0.5) – 50% of particles are smaller than this diameter (median diameter); d(0.9) - 90% of particles are smaller than this diameter. $^{a-d}$ Significant difference between the virgin and used powder ($P \leq 0.05$).

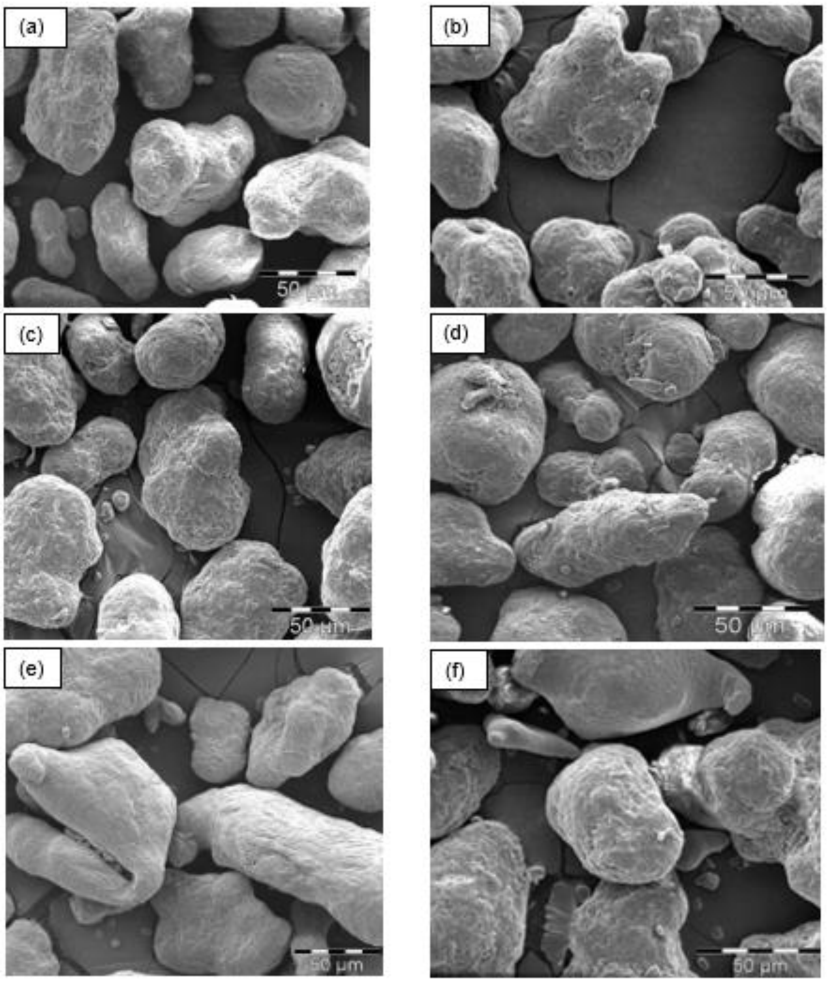

Figure 1: SEM images of a) virgin nylon from Facility A, b) used nylon from Facility A, c) virgin nylon from Facility B, d) used nylon from Facility B, e) virgin alumide from Facility A and f) used alumide from Facility B.

XRF analyses of virgin alumide powder from Facility A detected that 40.98% of the powder sample contained metals, of which 39% was aluminium. The used powder from Facility B contained

53.49% metals, of which 51% was aluminium. All virgin and used nylon samples contained less than 4% metals.

3.2 Area particle emissions

Figure 2a-f illustrates samples collected during each of the three phases of AM with a TSI Model 3007 Condensation Particle Counter (CPC) (TSI Inc., Shoreview, Minnesota, USA) and a TSI AeroTrak^{TM} Airborne Particle Counter (APC) (TSI Inc., Shoreview, Minnesota, USA). During these three phases of the SLS process, nylon-12 (PA2200) was used, but different builds were manufactured. Figure 2a indicates an increase in particle number concentration above the ambient during the period when the machine was cleaned, powders were mixed and powder bins were refilled (pre-processing). A maximum particle number concentration of 1.6×10^{10} p/m^3 was detected during pre-processing for the 0.01 µm to > 1 µm particle size fraction. During machine cleaning a vacuum cleaner and brush were used to remove all excess powders in the machine from a previous build. Figure 2b supports the increase in particle number concentrations due to the activities performed by the AM operator during pre-processing. The highest particle number concentration was for the 0.30 µm particle size fraction, with a maximum of 1.6×10^6 p/m^3.

Figure 2c indicates a sudden increase in particle number concentration (3.7×10^{10} p/m^3) at approximately 136 minutes during the warm-up period of the machine. This increase was due to other nearby machines in the room that were opened. Figure 2c shows that when printing started, there was an increase in particle number concentration (0.01 µm to > 1 µm) compared to the ambient, but after a maximum was reached (3.5×10^{10} p/m^3) a decrease occurred. Figure 2d also confirms the increase in particle number concentration during the warm-up of the machine and the increase in particle number concentration when printing started, followed by a decrease. The highest particle concentration was 1.7×10^6 p/m^3 for the 0.30 µm size fraction. The increased levels of particle emissions during the warm-up of the machine were due to other machines also running during the sampling period.

Figure 2e and 2f indicate an increase in particle number concentration when the build was manually removed and when excess powder was removed with a brush and compressed air. Figure 2e indicates a maximum particle number concentration (0.01 µm to > 1 µm) of 1.0×10^{10} p/m^3, while the build is removed from the machine. Figure 2f illustrates a maximum particle number concentration of 1×10^6 p/m^3 for the 0.30 µm particle size fraction. All APC data indicate the emission of particles in the 0.30 µm and 0.50 µm size fraction, although the particles in the 0.30 µm were emitted in higher number concentrations.

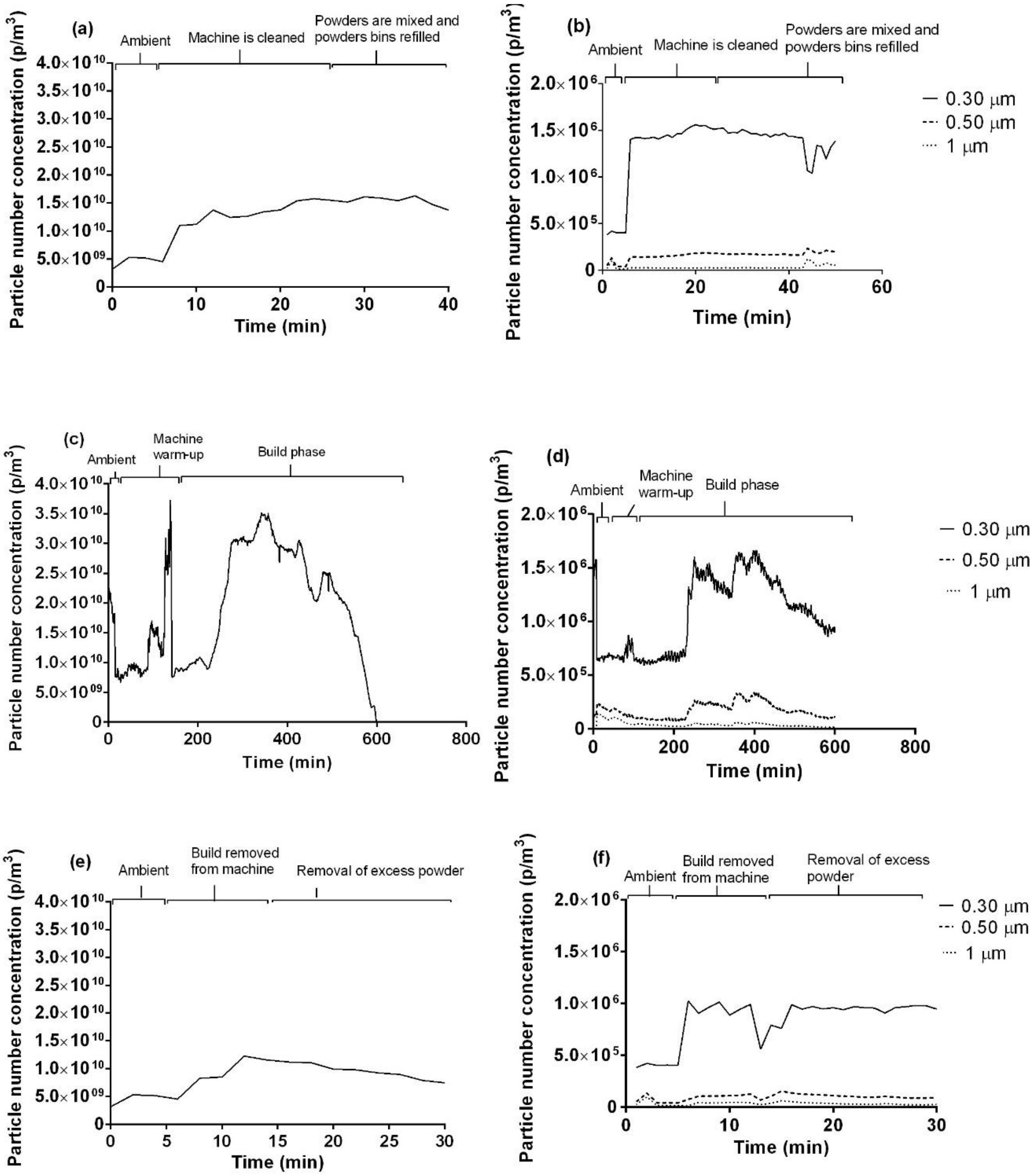

Figure 2: CPC measurements for a) pre-processing, c) processing and e) post-processing of nylon (PA 2200) at Facility A. APC measurements for b) pre-processing, d) processing and f) post-processing of nylon (PA 2200) at Facility A.

Table 2 shows that detectable concentrations of inhalable and respirable sized nylon dust were measured in the work area during SLS with nylon, while the airborne concentrations of inhalable and respirable sized alumide dust, in the work area during SLS with alumide, were below the limit of detection. The mean area emission of inhalable sized nylon dust during SLS with nylon was 0.54 mg/m^3, with a maximum concentration of 1.03 mg/m^3. The mean area emission of respirable sized nylon dust during SLS with nylon was 0.05 mg/m^3, with a maximum concentration of 0.08 mg/m^3.

Table 2: A summary of the emission of inhalable and respirable sized nylon and alumide dust at Facility A and B.

Powder	Size Fraction	Average Time (Min)	n	(mg/m^3)			n < BDL
				Min	**Mean***	**Max**	
Nylon (PA 2200)	**Inhalable**	322.5	4	BDL	0.54	1.03	3
	Respirable			BDL	0.05	0.08	
Alumide	**Inhalable**	256	2	BDL	BDL	BDL	2
	Respirable			BDL	BDL	BDL	

Min – Minimum; Max – Maximum; BDL – Below detection limit; For calculating the mean = values below detection limit was replaced by DL/$\sqrt{2}$; n < BDL indicates the number of samples below detection limit.

Two samples were collected to investigate the area emission of metals during SLS using alumide. The mean area emission of inhalable sized metal particles during the three phases, was 0.02 mg/m^3 for aluminium (Al), 0.006 mg/m^3 for iron (Fe), 0.002 mg/m^3 for titanium (Ti) and 0.004 mg/m^3 for zinc (Zn).

3.3 Area VOC emission

Table 3 indicates that acetone, pentane and naphtha emissions occurred during SLS, utilising nylon. The mean area emission concentrations, over three full shifts, of acetone, pentane and naphtha were 0.11, 0.09 and 6.14 mg/m^3, respectively. Naphtha was the VOC that had the highest area emission concentrations, with a maximum full shift concentration of 8.20 mg/m^3.

Acetone, pentane, chloroform, toluene and naphthas emission took place during SLS, utilising alumide. Naphthas was the VOC with the highest full shift emission, with a mean concentration of 3.62 mg/m^3.

Table 3: A summary of the full shift area emission of VOCs at Facility A and B.

Powder	VOC	Average Time (Min)	n	(mg/m^3)		
				Min	Mean*	Max
Nylon (PA 2200)	**Acetone**	268.3	3	0.07	0.11	0.15
	Pentane			0.07	0.09	0.11
	Naphthas			3.95	6.14	8.20
Alumide	**Acetone**	502	1	-	0.08	-
	Pentane			-	0.10	-
	Chloroform			-	0.04	-
	Toluene			-	0.03	-
	Naphthas			-	3.62	-

VOC – Volatile organic compound; Min – Minimum; Max – Maximum; BDL – Below detection limit; *For calculating the mean = values below detection limit was replaced by DL/$\sqrt{2}$.

3.4 Personal exposure monitoring

Table 4 indicates the exposure of AM operators to inhalable and respirable sized nylon and alumide dust during SLS utilising nylon and alumide, as well as exposure to particles < 300 nm. AM operator exposure to inhalable sized nylon dust during SLS with nylon during the three phases ranged between BDL and 11.29 mg/m^3. Detectable concentrations of respirable sized nylon dust were only found during post-processing (0.18 mg/m^3). The calculated TWA personal exposure to inhalable and respirable sized nylon dust for SLS with nylon was 2.30 mg/m^3 and 0.12 mg/m^3 respectively, while exposure to particles < 300 nm in all instances was BDL.

The personal exposure to inhalable sized alumide dust during SLS utilising alumide, during the three phases, ranged between 0.69 and 5.32 mg/m^3, while personal exposure to respirable sized alumide dust was only detected during post-processing (0.59 mg/m^3). The TWA personal exposure to inhalable and respirable sized alumide dust was 1.89 mg/m^3 and 0.17 mg/m^3 respectively. The mean exposure to particle < 300 nm was 0.095 mg/m^3, with a maximum exposure of 0.17 mg/m^3.

Table 4: A summary of the personal exposure to inhalable sized dust, respirable sized dust and particles < 300 nm at Facility A and B.

Powder	**Size Fraction**	**AM phase**	**n**	**Average Time (Min)**	**(mg/m^3)**		
					Mean*	**Min**	**Max**
Nylon (PA 2200)	**Inhalable**	Pre-processing	4	83.75	2.00	BDL	2.14
		Processing	3	136	BDL	BDL	BDL
		Post-processing	4	67.5	5.52	BDL	11.29
		Full Shift (TWA)	1	287.25	2.30	-	-
	Respirable	Pre-processing	4	83.75	BDL	BDL	BDL
		Processing	3	136	BDL	BDL	BDL
		Post-processing	4	67.5	0.18	BDL	0.21
		Full Shift (TWA)	1	287.25	0.12	-	-
	< 300 nm	Full Shift (TWA)	4	287.25	BDL	BDL	BDL
Alumide	**Inhalable**	Pre-processing	1	32	BDL	-	-
		Processing	1	360	0.69	-	-
		Post-processing	1	110	5.32	-	-
		Full Shift (TWA)	1	502	1.89	-	-
	Respirable	Pre-processing	1	32	BDL	-	-
		Processing	1	360	BDL	-	-
		Post-processing	1	110	0.59	-	-
		Full Shift (TWA)	1	502	0.17	-	-
	< 300 nm	Full Shift	2	256	0.095	BDL	0.17

Min – Minimum; Max – Maximum; BDL – Below detection limit; Mean exposure concentrations during phases were used to calculate an estimated TWA concentration; For calculating the mean TWA = values below detection limit was replaced by $DL/\sqrt{2}$; South African OEL of inhalable dust = 10 mg/m^3; OEL for respirable dust = 5 mg/m^3.

One sample was collected to investigate the personal exposure to metals experienced by the operators during SLS using alumide. The TWA personal exposure to metals, during the three phases, was 0.062 mg/m^3 for Al, 0.002 mg/m^3 for Fe, 0.002 mg/m^3 for Ti and 0.003 mg/m^3 for Zn. The TWA exposure to each individual metal was well below the South African time weighted average - occupational exposure limit - recommended limit (TWA-OEL-RL) concentrations. Personal Al exposure was higher than the area concentration (0.062 mg/m^3 vs. 0.02 mg/m^3), while the other metals detected had similar concentrations during area emission and personal exposure.

3.5 Personal VOC exposure

Personal exposure to acetone, pentane, chloroform and naphthas was detected during SLS with nylon and alumide. For nylon, chloroform exposure was detected only during the processing phase of one full shift, at a concentration of 0.04 mg/m^3. The maximum full shift TWA exposure concentrations, were 0.1 mg/m^3 for acetone, 0.05 mg/m^3 for pentane, 0.04 mg/m^3 for chloroform and 5.90 mg/m^3 for naphthas.

Personal exposure to acetone, pentane and napthas was detected during utilisation of alumide. The highest exposure to VOCs, was for naphthas, with a mean TWA concentration of 3.67 mg/m^3, over a full shift.

Table 5: A summary of the TWA full shift personal exposure to VOCs at Facility A and B.

Powder	**VOC**	**Average Time (Min)**	**n**	**TWA (mg/m^3)**			**OELs mg/m^3**
				Min	**Mean***	**Max**	
Nylon (PA 2200)	**Acetone**	268.3	3	0.04	0.07	0.10	1780
	Pentane		3	0.03	0.04	0.05	1800
	Chloroform		3	0.03	0.04	0.04	9.8
	Naphthas		3	2.67	3.94	5.90	2000 *
Alumide	**Acetone**	502	1	-	0.10	-	1780
	Pentane		1	-	0.08	-	1800
	Naphthas		1	-	3.67	-	2000 *

VOC – Volatile organic compound; Min – Minimum; Max – Maximum; BDL – Below detection limit; For calculating the mean TWA = values below detection limit was replaced by DL/$\sqrt{2}$; South African TWA-OEL-RL are used; * Occupational Safety and Health Administrative, USA – Permissible Exposure Limit.

4. Discussion

The aim of this study was to determine the physical and chemical characteristics of virgin and used nylon-12 (PA2200) and alumide and to determine the area emission of and personal exposure to HCSs (particulates, metals and VOCs) during SLS with nylon and alumide.

Both PSD and SEM analyses indicated that the particle sizes for both virgin and used nylon and alumide fell into the inhalable particle size fraction, which means it can penetrate to the mouth and nose (CEN, 1993; Brown *et al*., 2013). Although PSD results indicate that virgin and used powders fell into the inhalable particle size range, the particle counters and gravimetric sampling indicated that submicron particles are present during the three phases of SLS utilising nylon and alumide. There were no significant differences between the volume weighted mean sizes of virgin and used nylon, although there were statistical significant differences found between the PSD of virgin and used nylon [d (0.1), d (0.5) and d (0.9)] at Facility A and nylon [d (0.1)] at Facility B. The SEM results indicate no visible difference in the particle size or shape of virgin and used nylon. This shows that the SLS process only minimally influenced the size of the unsintered powders. At both Facility A and B, the particle sizes measured, for virgin nylon, were larger than the sizes indicated on the MDSs (A: 65.08 µm vs*.* 56 µm) (B: 64.99 µm vs*.* 56 µm). Measured virgin alumide powders were slightly larger than that indicated by the MDS (63.85 µm vs. 60 µm). These discrepancies lead to suspicions regarding the validity of the MDS's used. Inaccurate information, such as the above could have both manufacturing and health consequences if operators do not receive the correct information from the manufactures. The particle size and PSD of AM powders are two important properties focussed on during PBF to ensure that a product of superior quality is delivered, having a smooth surface finish and satisfying specific density (Sutton *et al.,* 2016). In addition, inaccuracies as identified could potentially lead to implementation of incorrect control measures and misinterpretations of which health effects could possibly arise from respiratory exposure during AM.

As indicated by all representative CPC and APC samples (Figure 2a-f) there is an increase in particle number concentrations during the three phases of AM, when compared to the ambient readings. In figure 2a and 2b particle number concentrations increased when the machine was cleaned, powders were mixed, and powder bins were refilled. The maximum particle number concentrations for the 0.01 µm to > 1 µm particle size fractions were 1.6 x 10^{10} p/m^3 and 1,0 x 10^6 p/m^3 for the 0.30 µm size fractions. Figure 2c and 2d both indicated a sudden increase in particle number concentration (3.7 x 10^{10} p/m^3) during the warm-up of the machine due to other machines that were opened. An increase in particle emission was observed when printing started, until a maximum was reached (3.5 x 10^{10} p/m^3), followed by a decrease in particle number concentration. Kwon *et al*. (2017), Stabile *et al*. (2016) and Zhang *et al.*, (2017) all reported that there was an increase in particle emission during the processing phase followed by a decrease. However, these studies focussed on the particle emission rates (p/min) and could not be compared to values of this study. The reason for higher particle number concentrations during the processing phase, compared to the other two phases, is that other processes were running at the same time in the room where measurements were taken. Figure 2e and 2f indicate an increase in particle number concentration when the build was manually removed, and excess powders were removed with a brush and compressed air. All APC results indicate the emission of 0.30 µm and 0.50 µm particle size fractions, although during the three phases the highest number concentrations were found for the 0.30 µm particle size fraction. Graff *et al.* (2016) also identified higher emission rates while manually handling metal powders during activities, such as vacuum cleaning, handling the build plate, metal powder streaming and loading of powders into the machine. Therefore, the particle number concentration is determined by the type of activities that take place during each phase, such as machine cleaning, powder mixing, removal of the build from the machine, the removal of excess powders and is also influenced by surrounding machines or activities performed in the same printing area.

As indicated in Table 2, the area emission of inhalable and respirable sized nylon dust, over a full shift, was low overall and only one of the four samples indicated concentrations above the detection limit. The mean inhalable and respirable sized nylon dust emission was 0.54 mg/m^3 and 0.05 mg/m^3 respectively, while the maximum emission of inhalable and respirable sized nylon dust during the sample with detectable levels was 1.03 mg/m^3 and 0.08 mg/m^3. Inhalable personal exposure results in Table 5, indicates that the highest concentrations of exposure to nylon dust took place during the post-processing phase, with a mean concentration of 5.52 mg/m^3. The maximum exposure to inhalable nylon dust was 11.29 mg/m^3, which took place over 70 minutes during the post-processing phase. Although it cannot be compared to the OEL, which legislates exposure over an 8-hour shift, it is still a concern that such high concentrations of exposures were experienced for specific tasks. APC and CPC results also illustrated that there is an increase in particle number concentration from the ambient during post-processing activities. During these post-processing activities, the AM operator removed the build from the build chamber and then manually removed most of the unsintered powders. After most of the powder had been removed, compressed air was used inside a fully enclosed chamber with a local extraction ventilation (LEV) system. The use of compressed air does not only increase the risk of area emission and personal exposure but is also prohibited according to Regulation 13 of the HCSR (HCSR, 1995). Following the post-processing phase, the pre-processing phase also revealed detectable levels of exposure to inhalable sized nylon dust (2.0 mg/m^3), but it was not as high as the post-processing concentrations. There are no national or international OELs for nylon and therefore personal exposure results were compared to the OELs of inhalable and respirable dust found in the HCSR. All full shift personal exposure measurements were below these OELs.

The personal exposure to respirable sized nylon dust also indicated the highest exposure concentrations during the post-processing phase, with a mean concentration of 0.18 mg/m^3. Although PSD results indicated that all nylon powder fell into the inhalable range, it is indicated here that AM operators were exposed to respirable fractions of nylon particles, but the concentrations were much lower than the OEL. The concentrations of full shift personal exposure to inhalable and respirable sized nylon dust were well below the OELs. The personal exposure results for nylon dust actually indicated higher concentrations than those of the area emission. This could be because the AM operator is in close contact with the powders. Therefore, area emission samples should never be used in isolation to evaluate the personal exposure of AM operators. Graff *et al*. (2016) also found increased particle emissions and exposure during pre- and post-processing activities, such as vacuuming and handling of the metal plate, metal powder streaming and machine cleaning and loading. Johannes *et al*. (2016) indicated that exposure to nylon fibres can lead to a rare form of pneumoconiosis. It is important to consider that although nylon does not have a specific OEL, exposure should be kept as low as possible in order to reduce the risk of developing adverse health effects.

All area gravimetric emission results of inhalable and respirable sized alumide dust were below detection limit. Very low concentrations of Al, Fe, Ti and Zn were detected during ICP-AES analysis of alumide samples. Because alumide is a combination of aluminium and polymer powder, the detection of Al was expected. The rest of the metals detected could be due to cross-contamination, because both facilities work with other AM processes and materials. XRF analyses also confirm that virgin alumide powders consist of 39% aluminium, while used alumide consist of 51% aluminium. The highest concentration of personal exposure to alumide dust takes place during the post-processing activities, with concentrations of 5.32 mg/m^3 for inhalable fractions and 0.59 mg/m^3 for respirable fractions. A concentration of 0.062 mg/m^3 of Al was detected in personal monitoring samples of SLS utilising alumide. The same post-processing activities took place, as mentioned above for nylon. For pre-processing the personal exposure to inhalable sized alumide dust were below levels of detection, while processing actually indicated detectable levels of exposure (0.69 mg/m^3). This could be because the AM operator had to open the machine during the processing phase, to adjust the powder bed inside. Personal exposure to alumide particles < 300 nm was also detected (0.095 mg/m^3). Although the mean concentration for particles < 300 nm was very low it should be noted that operators experienced personal exposure to these small particles and that measures should be implemented to protect them from possible exposure.

Detectable concentrations of acetone, pentane and naphthas were found during area emission and personal exposure monitoring during SLS utilising nylon, although the detected concentrations of the all VOCs were low. The presence of very low concentrations of chloroform during the personal VOC monitoring could be due to the chemicals used to clean the AM machines. Area emission and personal exposure monitoring during SLS utilising alumide found detectable levels of acetone, pentane and naphthas. All personal exposure concentrations were below the OELs of the individual VOCs (HCSR, 1995, NIOSH, 2007).

At both facilities there was a lack of adequate natural and mechanical ventilation in the rooms where powders were mixed and where SLS occurs. It is therefore recommended that a dust collection system, such as a local extraction ventilation system (LEV) should be considered, which will capture the particles at the source prior to emission into the air. A smaller portable LEV system would be beneficial, because the AM operator could move this system to the area where activities, such as powder mixing and cleaning of printed parts, are performed. The use of compressed air is strictly prohibited by Regulation 13 (a) of the HCSR (HCSR, 1995). It is therefore recommended that if compressed air is used, that it should only be used inside a fully enclosed cabinet to ensure that the particles do not become airborne in the general working area. According to Regulation 3 (1) of the HCSR (HCSR, 1995) all employers must fully train employees before they are exposed to HCSs. All AM operators must be fully trained in the risks of exposure and how to prevent exposure to HCSs. All AM operators at Facility A and B were fully equipped with effective PPE, including: half-face respirators, steel toe-capped shoes, overalls and nitrile gloves. At Facility A a dust mask (FFP2) with an active carbon moulded respirator was used, while at Facility B they used a full-face respirator with a combination filter (organic gases & vapours, inorganic gases & vapours, sulphur dioxide and particle matter). AM operators used their PPE during the pre-processing and post-processing phases and only when the machine doors were opened during processing. Operators should be trained and encouraged to wear their PPE while performing tasks where they are required to handle powder.

Prior to this study, no information was available regarding emission and exposure during SLS, utilising nylon and alumide and this study has confirmed that AM operators are exposed to HCSs during this process. Nevertheless, future studies should focus on collecting more data from the same builds. For example, if emission and exposure data can be collected from three processes that produce the same build then the differences in the emission and exposure during the three AM phases could be more accurately compared.

5. Conclusion

This study confirms the area emission of and personal exposure to HCS (particulates, metals and VOCs) during SLS, utilising nylon (PA2200) and alumide. PSD results showed that virgin and used nylon and alumide powders fell into the inhalable particle size range, however gravimetric analyses and particle counter monitoring indicated that AM operators were exposed to respirable as well as submicron particles. Direct reading particle counters indicate that the particle number concentrations increased, compared to the ambient, during the three phases of SLS utilising nylon. The personal exposure to inhalable and respirable sized nylon dust was below the respective OELs, although higher personal exposure concentrations were identified during post-processing activities, such as manual removal of the build, removal of excess powder and the use of compressed air. All inhalable and respirable area emissions for SLS utilising alumide were below detection limit, while personal exposure to inhalable and respirable sized alumide dust was the highest during post-processing activities. All VOCs emission and exposures were very low.

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CHAPTER 4: CONCLUDING CHAPTER

The following chapter contains the summary of the key findings of this study. The main aim and objectives of this study will be listed, and an indication of the successful achievement of these objectives will be given. The hypotheses formulated will be discussed as well as an indication given of acceptance or rejection of the hypotheses. The limitations of this study and the need for future studies will be argued.

4.1 Main Findings

This study investigated the respiratory exposure to hazardous chemical substances (HCSs) [particulates, metals and volatile organic compounds (VOCs)] during selective laser sintering (SLS) using nylon and alumide and contributes to the body of knowledge regarding risks associated with additive manufacturing (AM) processes. Particle size distribution (PSD) results indicated that both virgin (new) and used nylon and alumide powder fell into the inhalable particle size range (63.85 µm - 65.30 µm) as defined by the European Standard, EN481:1993 (Workplace atmospheres – Size fraction definitions for the measurement of airborne particles). Although inhalable sized particles were detected by PSD analyses, the results from the particle counters indicated the emission of submicron particles into the workplace air and personal exposure results showed personal exposure to respirable sized nylon and alumide dust during SLS utilising nylon and alumide. There were no statistical significant differences found between the volume weighted mean particle sizes of virgin and used nylon, and the scanning electron microscopy (SEM) analyses confirmed no visible changes in shape and size between the virgin and used nylon. Differences identified between the volume weighted mean particle sizes measured and those presented by the material data sheets (MDSs), for both nylon (65.08 µm vs 56 µm) from Facility A, nylon (64.99 µm vs 56 µm) from Facility B and alumide (63.85 µm vs 60 µm) from Facility A. X-ray fluorescent (XRF) analyses identified that virgin alumide consisted of 40.98% metals, of which 39% was aluminium, while used alumide consisted of 53.49% metals, of which 51 % was aluminium. The percentage aluminium content of the powder was not listed in the MDSs provided to the AM operators. It is very important that MDSs/safety data sheets (SDSs) contain correct and applicable information since the operators use the material data sheets to determine the potential health risk associated with use of the powder. Information such as particle size and powder composition are important since the size of a particle will determine the extent of penetration of these particles into the lungs (Brown *et al*., 2013). In addition, chemical composition influences the particular health effects which might be caused by respiratory exposure. For example, excessive exposure to aluminium (Al) is associated with adverse health effects, such as Parkinson's disease, multiple sclerosis, dementia and cognitive deficiency (Kawahara *et al*., 2007; Exley, 2014).

As illustrated in Figure 2 (Chapter 3) particle number concentrations have increased from the ambient concentrations during all three phases of SLS, utilising nylon. This is an indication that all the phases of SLS could lead to increased exposure to submicron airborne particles. Assessments of results of personal exposure to inhalable sized nylon and alumide dust, during SLS, indicated that the highest concentrations of respiratory exposure took place during post-processing activities. Detectable concentrations of personal exposure to respirable sized nylon and alumide dust were only measured during post-processing activities which shows that this phase poses the highest risk to AM operators' respiratory health, since respirable particles can penetrate to the alveoli of the lungs (Brown *et al*., 2013). Particle number concentrations measured by direct reading instruments also confirmed increases in particle number concentrations during post-processing activities. Particles < 300 nm were also detected during SLS utilising alumide. All results for personal exposure to nylon and alumide were below occupational exposure limits (OELs) for inhalable and respirable dust. ICP-AES analyses showed aluminium, iron, titanium and zinc in personal exposure and area emission samples. Aluminium emission was caused by alumide powders that consist of nylon and aluminium, while the presence of other metals could be due to cross contamination from other AM processes. Additionally, the same gravimetric sampling methodology which was used to evaluate personal exposure was also used to measure the concentrations of inhalable and respirable sized particles in the workplace area. Results from these measurements were all below the limit of detection or very low, indicating that area monitoring cannot be used in isolation to assess personal exposure. VOCs detected during personal and area monitoring during SLS utilising nylon and alumide included naphthas, acetone, pentane, chloroform and toluene, but all these concentrations was well below the OELs (Table 5 of Chapter 3).

4.2 Further discussions

The main aim of this study was to determine the physical and chemical characteristics of powders as well as the emission of and personal respiratory exposure to HCSs (particulates, metals and VOCs) emitted during SLS, utilising nylon and alumide powders, at two AM facilities in South Africa. This overall aim has been achieved through the realisation of three objectives.

The first objective was to assess the physical characteristics (size and shape) and chemical composition of virgin and used nylon and alumide powders from two AM facilities. This objective was achieved through PSD, SEM and XRF analyses of both virgin and used nylon and alumide as discussed in section 4.1.

The second objective was to assess the airborne concentration of particulates (inhalable, respirable and submicron), metals and VOCs emitted during the three phases of SLS, utilising nylon and alumide powders. This was achieved through condensation particle counter (CPC), airborne particle counter (APC), gravimetric sampling and VOC badges. All CPC and APC results indicated that there was an increase in particle number concentrations from the ambient during all three phases of SLS utilising nylon. These two particle counters indicated the emission of various particle sizes (0.01 µm to > 1µm) in the workplace atmosphere. Increases were identified during manual handling of powders during pre-processing as well as post-processing activities, such as machine cleaning, powder mixing, refilling of powder bins, removal of the build and removal of excess powder. Graff *et al.* (2016) also reports the increase in particle emission when metal powders were manually handled during vacuum cleaning, handling the build plate, machine cleaning and loading of powders into the machine. For the current study, during machine cleaning and loading of powders into the AM machine for SLS utilising nylon, the maximum particle number concentrations for 0.01 µm and > 1µm sized particles were 1.6 x 10^{10} p/m^3 and for 0.30 µm sized particles was 1.5 x 10^6 p/m^3. An increase was also identified during the warm-up of the AM machine up to a specific peak (3.5 x 10^{10} p/m^3 for 0.01 µm and > 1µm sized particles and 8,0 x 10^5 p/m^3 for 0.30 µm sized particles), followed by a decrease. It should be noted that these particle number concentrations may have been caused by other processes also running in the surrounding printing area. Kwon *et al*. (2017), Stabile *et al*. (2016) and Zhang *et al.*, (2017) also identified that there is an increase in particle emission after printing started, up to a peak, followed by a decrease. This same pattern was observed in the particle emission during this study. Even though PSD results indicated all nylon powders fell into the inhalable particle size range (63.85 µm - 65.30 µm), the CPC (0.01 µm to > 1µm) and APC (0.30µm) direct reading instruments had both indicated that submicron sized particles were emitted into the workplace air during SLS, which increases the risk associated with the process. All area gravimetric samples for inhalable and respirable sized nylon dust was very low, while all samples for inhalable and respirable sized alumide dust was below detection limit (BDL). Acetone, pentane, toluene and napthtas were the detected VOCs during SLS, utilising nylon and alumide, but all these concentrations were very low.

The third objective was to assess the concentration of particulates (inhalable, respirable and submicron), metals and VOCs that AM operators were exposed to, during the three phases of SLS, utilising nylon and alumide. This objective was reached through personal respiratory sampling using gravimetric methods as well as VOC sampling badges. The results for SLS utilising nylon and alumide indicated that the highest mean concentrations of personal exposure to inhalable and respirable sized nylon and alumide dust took place during post-processing activities (5.52 mg/m^3 and 5.32 mg/m^3, respectively). Exposure to respirable sized nylon and alumide dust was only found during the post-processing phase (0.18 mg/m^3 and 0.59 mg/m^3), while the concentrations for the other two phases were BDL. Although PSD indicated that nylon powders fell into the inhalable particle size range, it is here indicated that personal exposure to respirable sized particles also occurs, although the concentrations were well below the OEL. Personal exposure to particles < 300 nm was identified during the use of alumide. Acetone, pentane, chloroform and naphthas were the VOCs identified during both SLS utilising nylon and alumide, but the concentrations were below the OELs. Although the concentration of chloroform was below the OEL (0.41% of TWA-OEL-RL), it should be noted that chloroform is identified as a Group 2B carcinogen, meaning that it “is possibly carcinogenic to humans” (IARC, 1999) and exposure should be kept as low as possible.

Two hypotheses were formulated for this specific study. The first hypothesis was that HCSs (particulates, metals and VOCs) are emitted into the workplace atmosphere where SLS, utilising nylon and alumide powder, takes place. This study indicated that particles in various size fractions were emitted into the workplace, but in very low concentrations. CPC and APC results shown that during the three phases of SLS utilising nylon there is an increase in the particle number concentration (0.01 µm to > 1µm) from the ambient concentration. The particle counters also indicate that an increase in the particle number concentrations has occurred during certain activities, such as, machine cleaning, powder mixing, refilling powder bins, warm-up of the machine, removal of the build and removal of excess powders. Gravimetric sampling indicated that inhalable and respirable sized nylon dust is emitted over a full shift. ICP-AES results of alumide samples showed aluminium, iron, titanium and zinc were all released into the workplace during SLS with alumide. Acetone, pentane, chloroform, toluene and naphthas were emitted during SLS while utilising nylon and alumide, although all concentrations were very low. However, all gravimetric area samples collected during SLS with alumide was below the limit of detection for the method. Therefore, this hypothesis is partially accepted since the study has shown that HCSs (particulates, metals and VOCs) are emitted into the workplace where SLS, utilising nylon and alumide, takes place although area emissions of inhalable and respirable sized particles was not detected.

The second hypothesis was that AM operators experience personal respiratory exposure to HCS (particulates, metals and VOCs) during SLS with nylon and alumide powder. Personal exposure to inhalable sized nylon and alumide dust was detected during SLS, utilising nylon and alumide. The highest concentration of exposure to inhalable sized nylon and alumide dust was found during post-processing activities. Personal exposure to respirable sized nylon and alumide dust only took place during post-processing activities, which is an indication that this phase poses the greatest health risk. The personal exposure samples collected during SLS with alumide, also contain aluminium, iron, titanium and zinc, although these concentrations were below OELs. All particulate concentrations detected from both SLS utilising nylon and alumide was below the

OELs for total inhalable and respirable dust. Acetone, pentane, chloroform and naphthas was detected during the SLS utilising nylon and alumide. All these concentrations were below the OELs given in Table 5 (chapter 3). Therefore, this hypothesis is accepted, because personal respiratory exposure to HCS (particulates, metals and VOCs) during SLS with nylon and alumide occurred during this study.

4.3 Limitations of the study

There is very little information available regarding emissions and exposure during SLS, utilising nylon (PA2200) or alumide. There are also very few facilities that make use of these materials during SLS and each facility usually only have two AM operators, who are multi-skilled and trained in various AM technologies. Therefore, it was not possible to include more AM operators. Additionally, nylon and alumide objects were printed by order and due to time and availability constraints, it was not possible to collect more samples during SLS, utilising nylon and alumide.

4.4 Recommendations

When considering control measures, it is important to ensure that these measures will be effective in reducing the emission of and exposure to HCSs (particulates, metals and VOCs). According to the hierarchy of control, elimination should be considered first, followed by substitution, engineering controls, administrative controls and lastly personal protective equipment (PPE) (HSE, 2013). The elimination of the emission of or exposure to nylon and alumide powders would be the most effective way of reducing any health risks. In this case the elimination of the contact between the AM operators and the powders they are exposed to, is not possible. To substitute the powders used is also not possible, because these powders are very carefully chosen according to their physical and chemical properties.

Engineering Control Measures

At both facilities a lack of natural and mechanical ventilation was observed in the rooms where SLS machines were located and where powders were processed. It may be beneficial to make use of dust collection systems, such as a local extraction ventilation system (LEV), which captures particles before they become airborne (Cecala *et al*., 2012). Smaller portable LEV systems can also be used, which enable the AM operator to move the system to the area where the worked is performed. Portable LEV systems will especially be useful during pre- and post-processing activities to ensure that exposure is kept as low as possible. During the pre-processing activities, such as powder mixing, there was no extraction systems used and it caused a lot of powders to become airborne. Various surfaces, such as the floor, were visually contaminated with powder, which could become airborne again. During post-processing activities the build was manually removed, and excess powder was removed using a brush, which caused much of the powders to become airborne. A notable quantity of the powders was also spilled during removal of excess powders. The use of the LEV system in these instances will ensure that these powders are captured before becoming airborne and settling on surrounding surfaces. The inlet of the portable LEV system could be placed in the door at the bottom of the AM machine when the machine is cleaned and build is removed. It can then be placed on the table where the post-processing takes place, to ensure that particles are captured before being released into the air.

Isolation or enclosure of the AM process or machine may lower the exposure of the AM operators. At Facility A various AM machines were located in the same room, which lead to higher concentrations of particles in the air, as indicated by the results of the particle counters during the processing phase of SLS with nylon. During this phase there was a peak particle number concentration, which was possibly caused by other machines running. At Facility B there were only two AM machines located in the same room, proving to be a more effective measure to ensure isolation.

Both Facility A and B made use of compressed air inside an enclosed chamber. At Facility A, the compressed air was also used outside of the enclosed chamber, after the greater quantity of powder was removed from inside the chamber. The use of compressed air is strictly prohibited by Regulation 13 (a) of the HCSR (HCSR, 1995). Therefore, it is recommended that compressed air should only be used inside an enclosed chamber (glove box) in order to protect the operator against exposure.

Administrative control measures

It is recommended for both Facility A and B that the cleaning protocols should be improved, because not all surfaces were cleaned effectively. Vacuum cleaners were used to clean most of the powder on surfaces, but certain areas were not cleaned of spilled powder, especially in the rooms where post-processing activities, such as removal of excess powder, took place. After each build has been finished, all surfaces should be cleaned by using a vacuum cleaner with a water filtration system, to ensure that there is not a build-up of powder. It is also recommended that after most powder have been removed, a wet cloth is used to remove the rest of the powders, because this will also safeguard against the powder becoming airborne.

Good personal hygiene practices are very important to reduce the exposure of AM operators to HCSs. Dirty PPE should be removed before the AM operator enters other areas, such as offices or kitchens, to ensure that other areas are not contaminated with powders. Proper change rooms must be provided where the operators can remove all contaminated PPE, before leaving the printing area. Hyslop *et al.* (2017) found metal powders in non-printing areas of AM institutes, such as offices and kitchens which emphasises that good hygiene and decontamination practices should be implemented to prevent workers from the entire AM facility ingesting powder in the kitchens or becoming unnecessarily exposed in offices.

According to Regulation 3 (1) of the HCSR (HCSR, 1995) all employers must adequately train and educate their employees before they are exposed to HCSs. Information regarding the following aspects should be provided:

- The potential sources of exposure.
- The potential adverse health effects that could be caused by exposure.
- The control measures in place to reduce exposure.
- The proper use and decontamination of PPE.
- The proper method of cleaning.

The operators must be fully aware of the HCSR (HCSR, 1995) to guarantee their accountability regarding their own responsibilities and prohibitions while working with HCSs.

PPE

The following PPE was worn by AM operators at Facility A:

- Dust mask: DroAir EN 149:2001 + A1:2009 FFP2, with an active carbon moulded respirator (disposable).
- Steel toe-capped shoes.
- Overalls
- Nitrile gloves

The following PPE was worn by AM operators at Facility B:

- A full-face respirator with a combination filter (organic gases & vapours, inorganic gasses & vapours, sulphur dioxide and particle matter)
- Steel toe-capped shoes.
- Overalls
- Nitrile gloves

Revaluation of current PPE should be undertaken to ensure that sufficient protection from the HCSs present is provided. A N95 respirator should be considered, because it filters up to 95% of 0.30 micron sized particles (FDA, 2018). Contaminated clothing should be cleaned with a vacuum cleaner to remove all loose powders. It is important that the last piece of PPE to be removed, is the respirator. Operators should never leave the printing area still wearing any contaminated PPE, to reduce contamination of other surrounding areas. AM operators should also clean the PPE after each build, because accumulation of powders on PPE was observed at both facilities.

4.5 Future studies

This study has confirmed that emission of and exposure to HCSs (particulates, metals and VOCs) takes place during SLS utilising nylon and alumide. Future studies should focus on collecting data from multiple prints where exactly the same object is built three to four times, to provide more detailed information and a better understanding of the respiratory exposure that should be expected during SLS, utilising nylon and alumide.

4.6 References

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